CELLULOID

ITS RAW MATERIAL, MANUFACTURE, PROPERTIES AND USES

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WITH SIXTY-NINE ILLUSTRATIONS

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PREFACE

Celluloid is such a well-known product and appears to us in so many forms in everyday life that we are apt to take it for granted without bestowing much attention on it, and yet not many years ago celluloid was quite unknown, and our immediate ancestors had to be content to use the natural products with which it now more than competes.

It would be a difficult problem to enumerate all the purposes to which celluloid has been applied, but it is used in place of ivory, tortoiseshell, bone, and horn for knife-handles, umbrella-handles, combs, boxes, buttons and ornamental trinkets generally. For this reason it has been known as imitation ivory, imitation tortoiseshell and so on, and this application of the word imitation to it has very largely detracted from its value in the view of those who are æsthetically inclined, the word "imitation" being abhorred by artists generally. From a practical point of view, however, celluloid exhibits so many useful properties that it has made for itself a place in industrial and everyday life.

Celluloid is a product of nitro-cellulose, and being allied to gun-cotton, is regarded as highly dangerous and as likely to explode if heated; but this is not the case. Although it is inflammable and will take fire when a flame is applied, it does not readily do so if ordinary care is taken, and under no conditions does it explode.

The history of celluloid is an interesting one, commencing with the discovery of nitro-cellulose by Braconnot in 1832, its conversion into collodion by Maynard in 1847, the use of collodion in photography by Scott Archer in

1850, and the preparation of plastic masses from it by Parkes, Spill, and Hyatt, and the final discovery of the value of camphor in such preparations which resulted in the celluloid of to-day.

In addition to its use for the purposes enumerated above, celluloid is employed in the manufacture of clear, colourless, transparent films for photography which have very largely displaced glass plates, and the roll films which are now so well known in the kinematographic halls all over the world. For the preparation of certain classes of varnishes, quite unaffected by air or moisture, celluloid has no equal, while a very important parallel industry—the artificial silk industry—also depends upon the raw product, nitro-cellulose, and therefore comes within the scope of the present work.

In this book, the raw product, cellulose, and its properties are first described, the preparation of the various nitro-celluloses then follows. Other raw materials, such as camphor, and also the solvents for nitro-cellulose and the methods of rendering it plastic occupy attention. A chapter is included upon the preparation of artificial silk, while subsequent chapters deal with the moulding of celluloid, preparation of celluloid varnishes, and other various applications for which celluloid has been found suitable. The final chapter is devoted to the chemical and physical examination of celluloid.

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CONTENTS

PAGES

INTRODUCTION 1–7

CHAPTER I

RAW MATERIALS FOR THE MANUFACTURE OF CELLULOID

Cellulose—Cellulose Esters—Cellulose Nitrates—Cellulose Acetates—Cellulose Xanthate—Gun Cotton—Preparation of Gun Cotton—Special Gun Cottons for Celluloid Manufacture—Nitrating Centrifugalizers—Collodion Cotton 8–46

CHAPTER II

OTHER RAW MATERIALS

Camphor—Japanese Camphor—Properties of Camphor—Artificial Camphor—Camphor Substitutes—Solvents—Diluents—Specific Gravity of Sulphuric Acid—Specific Gravity of Nitric Acid 47–68

CHAPTER III

THE MANUFACTURE OF CELLULOID

Historical—Manufacturing Celluloid by Heat and Pressure—Preparing Celluloid by the Cold Process 69–89

CHAPTER IV

MANUFACTURE OF ARTIFICIAL SILK

(Lustre-Cellulose—Glanzstoffe—Fil Brilliant)—Chardonnet's Process—Lehner's Process—Viscose 90–104

CHAPTER V

PROPERTIES OF CELLULOID 105–107

CHAPTER VI

TREATMENT AND APPLICATION OF CELLULOID

Celluloid Industry—Celluloid as a Basis for Artificial Teeth—Stained Celluloid Sheets as a Substitute for Glass—Celluloid Printing Blocks and Stamps—Metallic Incrustations—Imitation Florentine Mosaic—Celluloid Collars and Cuffs, etc.—Celluloid Films for Photography and the Kinematograph 108–146

CHAPTER VII

PAGES
RENDERING CELLULOID UNINFLAMMABLE . 147–151

CHAPTER VIII

EMPLOYMENT OF PYROXYLIN OR NITRO-CELLULOSE IN THE PREPARATION OF LACQUERS AND VARNISHES . . 152–162

CHAPTER IX

EXAMINATION OF CELLULOID 163–180

INDEX 181–188

CELLULOID

INTRODUCTION

THE progress of civilization, and the increasing requirements of all branches of trade and industry, have been accompanied by a growing scarcity of many raw materials, the prices of which have risen in consequence. For this reason numerous attempts have been, and are being, made to imitate certain raw materials on the one hand, and on the other to find other materials capable of replacing them for many of the purposes to which they are applied. Thus, endeavours have been made to imitate ivory and caoutchouc and also tortoise-shell, horn, amber, etc., the earliest success in this direction being that obtained by Parkes of Birmingham, who introduced the substance known as Parkesine, used as a substitute for ivory and caoutchouc. This product being as hard as horn, and yet as flexible and supple as leather, and capable of replacing ivory and mother-of-pearl as well as caoutchouc and gutta-percha, was the first of its kind to arouse general interest.

Parkesine is interesting since it is the forerunner of celluloid, and its preparation and application are therefore worthy of close attention. The inventor prepared this product by mixing anhydrous wood naphtha with gun-cotton, and thus obtained a solution suitable, according to its consistency, for purposes ranging from waterproof clothing to the insulation of telegraph wires, manufacture of tubes, etc. To ameliorate the hardness and brittleness, which unfitted it for certain purposes, the product was kneaded with castor oil, cotton-seed oil, or other fatty oils: a mixture of the gun-cotton solution and castor oil, for instance, furnishing a composition specially adapted for coating telegraph wires and water-proofing textile fabrics.

Subsequently improvements were introduced, consisting in the employment of collodion dissolved in wood spirit mixed with drying oils, treated according to the degree of elasticity required with 2 to 10 per cent. of sulphur chloride, together with an addition of carbon disulphide to check the violence of the reaction, the resulting product being incorporated with varying proportions of dissolved gun-cotton, which, according to the result desired, seldom exceeded 20 per cent. By warming, this mass is converted into a pasty condition, enabling it to be moulded into any desired shape. The products obtained in this way were very handsome, and included sheets in various colours, imitation marble patterns, combs, knife handles, etc. The solvent employed facilitated the introduction of various colouring agents (coal-tar dyes in particular) into the mass; while powdered colours could also be incorporated by rolling or kneading.

For some years Parkesine enjoyed a fair amount of popularity in England, but was too expensive to retain that position for long; and it was not until 1867, when Spill invented xylonite, and in 1869 that the invention of celluloid by the brothers Hyatt, who were printers at Newark in the State of New Jersey, opened up a new era in this class of preparations. The discovery was arrived at in the course of experiments concerned with the production of a printer's roller material capable of withstanding atmospheric influences. The experiments were made with collodion, and it was found that by suitably treating this substance with camphor an entirely new product, possessing very valuable properties, was produced. The name "celluloid" was given to it on account of cellulose forming the raw material.

Although in the first edition of this work a future was foretold for this product, it could not be foreseen at that time that such an important industry would be developed from it. In fact in the early stages a considerable amount of scepticism was shown by many people as to the value of celluloid, and a certain amount of interest therefore attaches to opinions which were expressed at that time.

Thus, the brothers Dobler, makers of hard rubber and celluloid articles in Berlin, stated their belief that the good qualities of celluloid would be of but little avail, owing to the unreasonable prejudice against it and the half-hearted attempts made to introduce it into the various branches of industry. It was also rendered unpopular by newspaper articles inspired by competing interests and containing foolish statements put forward with the greatest seriousness, the effect being the greater since these assertions were also disseminated by leading journals and even by trade organs. One of these statements was to the effect that "the idea that there is any future at all for celluloid is now banished from the minds of manufactures and traders."

Another firm of celluloid makers gave a more favourable opinion, having written to the author as follows: "It is possible that celluloid will not retain its present popularity, more especially in view of the undiminished agitation against it on the part of interested persons; but it will never, as is often prophesied, entirely disappear, its prominent position along with ivory, tortoise-shell, hard rubber, etc., being assured." Professor Reuleaux, however, held opposite views. He averred that "it is unnecessary to employ this substance for purposes of imitation in order to render it popular. As a matter of fact, celluloid needs handling very carefully in connection with industrial art. It would be easy to deviate with this new substance into the by-path of imitation, that insidious evil which has already done so much injury to our industries that friends of industrial art shudder when they hear of a new 'successful imitation' being introduced. Manufacturers cannot be too urgently warned against this habit of imitation, which is always attended with the danger that what is really capable of accomplishment is lost sight of in attempts at the unattainable. If we wish to make a good article, we must strive after the truth and not after imitations: that is to say, given a good material, we should endeavour in its industrial application to develop it to the extent which its inherent properties permit. In this way we shall obtain better results than by imitation, which at best always infers a certain inferiority."

Against this view, which contains a good deal of truth, must be set the fact that the materials to be imitated are so expensive that they are not within the means of all. In any case, however, in connection with the endeavours to produce good imitations of other materials by means of celluloid, it should not be forgotten that this led to great improvements in its manufacture and that the substance is of itself excellently adapted for utilization, without any attempt to pass it off in place of something else.

More than twenty years ago the high price of celluloid, owing to the imperfect methods of manufacture, imposed certain limits on its use, and at that time it could not possibly compete with natural products. At the present time the conditions are different, owing, on the one hand, to increased competition, and on the other, to improved methods of manufacture. The production of imitations by means of celluloid was, however, less with the idea of competing with individual materials than to demonstrate how universally applicable celluloid could be made. At the present time the production of certain imitations is justified, if only for the reason of their extreme cheapness, and because they can be worked in a far simpler manner than is possible in the case of many genuine materials.

For many branches of industry celluloid has become a really indispensable product, and one capable of extensive application.

The main objection at one time existing against the widespread use of celluloid was its inflammability and the rapidity with which it burns when brought near a flame. This, however, is the case with other materials, and it might be said, for instance, that no lady should wear a dress made of such inflammable material as muslin. Many lives have been sacrificed through the ignition of ladies' dresses, but no case is on record of lives being lost in this way through celluloid articles when properly used;

and, morever, these articles are for the most part very small and are certainly not used as clothing in the strict meaning of the term.

The only way in which celluloid can take fire is when it is brought into direct contact with flame, or has been heated to such an extent as to give off inflammable vapours; even then the presence of a flame is necessary to cause these vapours to ignite, or some special cause, such as the admixture of air with the vapours which are evolved during its manufacture.

The story about a billiard-ball that was ignited by contact with a lighted cigar lying on the edge of the table, and that set fire to the cloth before it could be removed by means of tongs, is a fable, this being impossible, which may be proved by trying the effect of a lighted cigar on celluloid.

Vapours that have been liberated from celluloid by contact with a glowing body will ignite on the approach of a flame, and the latter will then also attack the object, as in the case of a celluloid cigar-holder when the cigar has burned down into the holder.

Burning celluloid can be easily extinguished by a single strong puff of wind, unless the burning object has been on fire for some time. If a flame has just commenced to light a piece of paper, the latter can be blown out with ease; but if the whole of the paper has been attacked, blowing is no longer of any use. The same applies in the case of celluloid or any other burning object.

If the concentrated heat of a flame is allowed to act on celluloid, as for instance, when the latter is held over a petroleum lamp, the celluloid will ignite at a distance of about eight inches above the top of the lamp chimney. This is not surprising, since a piece of paper held in the same position will turn brown and give off a cloud of smoke. Under these conditions the celluloid first gives off vapours, and then emits a slight, barely audible crackling noise. Immediately, a small flame appears twice in succession just above the surface of the celluloid, and the next moment the mass takes fire. In this case it is not the celluloid itself but the vapour that ignites, the flame then attacking the celluloid. Exactly the same thing can be observed with wood, though no one would think of raising objection to the use of wooden utensils on that account. Wood is a well-known material, whereas celluloid is comparatively new; and it is easy to understand that the opponents of this new product should desire to emphasize its defects and keep silent on the subject of its advantages.

From what has been said, it will be evident that celluloid articles can only be ignited when they are held in a flame or have been heated sufficiently to decompose the material. Therefore, wearers of celluloid articles should take care not to go too near a flame, not from dread of the celluloid burning, but chiefly because of the risk of the hair or other parts of the body taking fire.

In any event, care should be exercised in selecting articles made of celluloid, as cigar- or cigarette-holders of this material may be really dangerous, owing to the ease with which it is decomposed in contact with the glowing tobacco when the latter is allowed to burn down too far. Should this result ensue, there is danger of the lips and mouth being scorched by the hot vapours.

Particular care is necessary when celluloid is stored in large quantities, and when the material is being worked in the lathe, etc. Some time ago a number of fires broke out at short intervals in celluloid stores and workshops, the cause being attributed, in the former especially, to the liberation of celluloid vapours, though this could not be proved; and indeed it is hardly likely that, even with large quantities of celluloid, a sufficient volume of vapour would be liberated under such conditions to ignite explosively.

The case is different in workshops where celluloid is being worked, the fine dust given off filling the air of the room and forming a source of danger in view of the inflammable character of the material and the explosive nature of organic dust (*e.g.* flour in flour mills).

In the course of years the public has gradually learned that celluloid is not really more dangerous than many other articles in general use; the best proof of this being the widespread application of this substance for many articles of use, toilet articles, etc., and also for industrial purposes. If there were any undue risk, or any danger greater than we are exposed to daily, celluloid would not have become so popular.

Moreover, in the course of the last few years, innumerable methods have been proposed for replacing the expensive ingredient, camphor, by uninflammable materials, and to introduce into celluloid substances capable of greatly diminishing (if not entirely removing) its inflammability, thereby considerably lessening the risks attending the storage, working and use of the material. Finally, there are now in the market materials, like galalith from milk casein, that have all the appearance of celluloid and are quite uninflammable.

CHAPTER I

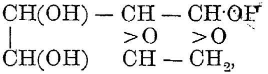
RAW MATERIALS FOR THE MANUFACTURE OF CELLULOID

CELLULOID may in general—or at least it could until recently—be described as a composition consisting of more or less nitrated pure cellulose and camphor rendered plastic, or dissolved in various solvents, mechanically treated, stained any desired colour with dyestuffs or pigments, and obtained, after the evaporation of the solvents, in the form of solid blocks, plates, sheets and rods, which may be worked up into a great variety of useful articles. The manufacturers of celluloid, who are comparatively few in number, restrict themselves to producing this material (and xylonite), whereas the numerous makers of celluloid articles work up the product by moulding, pressing, or turning it in the lathe, etc.

Before describing the manufacturing process, which has undergone extensive modification through the introduction of substances intended to supersede camphor to a smaller or greater extent, it will first be necessary to treat of the raw material, cellulose and its derivatives, nitrocellulose (gun-cotton, collodion, etc.) so far as it may be necessary to make the subject easily understood.

Cellulose is the basic framework of woods and vegetable tissues in general. In a pure state it is a carbohydrate, having the same empirical formula as starch and dextrin ($C_6H_{10}O_5$), although differing materially from both these in its properties. It has not hitherto been possible to determine the molecular weight of cellulose, but from a consideration of its reactions this is probably fairly high.

It is usual to express the formula as $(C_6H_{10}O_5)_n$, and Prof. Green suggests the following graphical representation



$$\begin{array}{lll} CH(OH) - & CH - & CH{\cdot}OH \\ | & >O & >O \\ CH(OH) & CH - & CH_2, \end{array}$$

which indicates an inner anhydride of glucose, into which latter it is converted by hydrolysis; the three hydroxyls (OH) being also replaceable by other groups, for instance, in the formation of the nitrates, acetates and other derivatives.

The theoretical percentage composition of cellulose is

	Composition of Pure Cellulose.
Carbon .	. 44·43
Hydrogen	. 6·13
Oxygen	. 49·41
	100·00

Pure cellulose is, however, difficult to prepare, the nearest approach to it in commerce being bleached cotton fibre and the highest grades of filter paper which approximate in composition to the above figures. In unbleached cotton there are always present small quantities of pectin, gum, wax, fat, and mineral constituents, as may be seen from the following figures given by the Tennessee Experiment Station :—

	Composition of Raw Cotton.	
	Minimum.	Maximum.
Water	6·74	8·0
Cellulose	83·71	87·0
Organic matter (including albuminous matter, carbohydrates, wax, and fat .	4·0	7·9
Fat	0·61	
Protein	1·50	
Carbohydrates	5·79	
Mineral matter	1·0	1·65

The ultimate composition of cotton, after deducting the ash, is given below:—

	Gladstone.	Ransome.	Schmidt and Hecker.	Pettenkofer.
Carbon . . .	44·37	44·20	43·27	44·5
Hydrogen . .	7·24	7·04	6·30	6·1
Oxygen . . .	48·39	48·76	50·43	49·4
	100·00	100·00	100·00	100·0

Wood is not a pure cellulose, but contains a considerable proportion of incrusting material known as lignin, termed by Cross and Bevan the "lignone complex," the proportion of true cellulose being 45–55 per cent. In the preparation of paper pulp from the softer woods, pine, spruce and fir, these incrusting materials are to a very large extent removed in solution by treatment with caustic soda or bisulphites, the more resistant cellulose being left behind in a purified state. This cellulose, however, reacts somewhat different to cotton cellulose. Then again we have the cellulose of the jute fibre, cuto-celluloses, and pecto-celluloses or hemi-celluloses, all of which have the empirical formula $C_6H_{10}O_5$, but different properties, so that Cross and Bevan, who are the authorities on this subject, conclude that the term "cellulose" embraces a number of different products, the cellulose of the cotton fibre being regarded as the typical cellulose, and it is this form with which we shall mostly have to deal.

Action of Reagents on Cellulose.—Cellulose usually shows the cellular structure of the vegetable matter from which it is prepared. It is a white, bulky material, devoid of odour or taste. It is quite insoluble in water, but absorbs water readily when wetted, giving it up again entirely on drying. Under normal conditions cellulose is hygroscopic, absorbing a small amount of water from the atmosphere; this may amount to from six to eight per cent., according to the humidity of the air and the temperature. There does not appear to be any chemical combination of the two with the formation of a hydrate, but the union is a physical one, a solid solution of the water in the colloidal cellulose.

Cellulose shows a considerable resistance to chemical action, thus it is scarcely acted upon at all by weak solutions of acids or alkalies. Organic acids, with the exception of oxalic acid, have no effect upon it; oxalic acid renders it brittle. Strong sulphuric acid chars it in the same way, as it does with sugar. Moderately concentrated sulphuric acid causes it to swell up considerably, forming hydrocellulose, which is coloured blue by iodine; by long-continued boiling it is converted into glucose. Concentrated hydrochloric acid also converts it into hydrocellulose.

Cellulose is entirely soluble in a concentrated solution of zinc chloride (50 per cent. solution), it is also dissolved by a solution of cuprammonium hydroxide (*i. e.* a solution of cupric hydroxide in strong ammonia) known as Schweitzer's reagent. From this solution it is reprecipitated by neutralization with an acid. This is the basis of the Willesden waterproof canvas, and the reaction will again be referred to under the section relating to artificial silk.

Strong solutions of caustic soda have a marked action upon cellulose (cotton), causing it to swell and contract, the fibres becoming changed from thin hollow tubes into stout solid filaments. This was the discovery of Mercer, the industrial treatment being known as "Mercerizing." In later years it was discovered that if the yarn was thus treated while under a state of tension, so that contraction could not take place, the resulting fibres had assumed a silky lustre. This process is now of considerable commercial importance.

CELLULOSE ESTERS.

Action of Nitric Acid, Cellulose Nitrates.—Dilute nitric acid behaves with cellulose in a similar manner to the other mineral acids; concentrated nitric acid, however, reacts with cellulose to form nitric esters, the so-called nitro-celluloses (pyroxylin, gun-cotton), the composition of which varies with the strength of the acid, the temperature, and the time of reaction.

The products of the reaction were at one time regarded as nitro-compounds, gun-cotton for instance being known as trinitrocellulose, and its formula expressed as

$$C_6H_7(NO_2)_3O_5,$$

but as these products do not respond to the reactions which are characteristic of the nitro-compounds, it is evident that they are nitric esters and their method of formation may be represented by the equation

$$C_6H_{10}O_5 + HNO_3 = C_6H_9O_4(NO_3) + H_2O.$$

Quite a number of cellulose nitrates have been described at different times, but they may be reduced to the following:—

Cellulose mononitrate .	$C_6H_9O_4(NO_3)$.	Percent. of nitrogen	6·76.
Cellulose dinitrate .	$C_6H_8O_3(NO_3)_2$.	,, ,,	11·11.
Cellulose trinitrate .	$C_6H_7O_2(NO_3)_3$.	,, ,,	14·14.

In the preparation of the cellulose nitrates it is, however, not possible to obtain any particular one in a state of purity. By the ordinary methods of preparation one nitrate merges imperceptibly into another, and there are no real breaks at which the reaction can be arrested, hence products containing any desired percentage of nitrogen can be formed by varying the three conditions, strength of acid, temperature, and time.

In the equation showing the formation of the cellulose nitrates it will be seen that water is a product of the reaction. This has the effect of progressively diluting the unaltered nitric acid so that the reaction slows down and finally stops. Also, as a result of this liberation of water, it is impossible to obtain the maximum effect of the nitric acid, the result being that the higher nitrates are not formed with nitric acid alone under ordinary working conditions.

It is necessary at this point to explain that in order to express the percentage results of analysis on a molecular basis it has been usual to assume that the cellulose molecule is of the magnitude $(C_6H_{10}O_5)_2 = C_{12}H_{20}O_{10}$, or $(C_6H_{10}O_5)_4 = C_{24}H_{40}O_{20}$. Cross and Bevan enumerate the cellulose nitrates on the basis of the C_{12} formula, while Berthelot, Vieille, and others have used the latter ratio. With the C_{12} formula there are six possible cellulose nitrates, and with the C_{24} formula there are twelve. It is probable that most of the nitrates described are merely mixtures of the three compounds which have already been mentioned.

With the highest concentration of nitric acid (*i. e.* 98 per cent.), and using dry cotton, the nitration usually stops at the stage represented by the tetranitrate $[C_{12}H_{16}O_6(NO_3)_4]$, only when the acid is in very large excess is the pentanitrate $[C_{12}H_{15}O_5(NO_3)_5]$ formed.

According to Vieille, the highest nitrate obtainable in this way is expressed by the formula $C_{24}H_{18}O_9(NO_3)_{11}$.

In his experiments Vieille * used a large excess of nitric acid—*i. e.* 100 to 150 times the weight of the cotton—in order to minimize the effect of the liberated water, the temperature was kept constant at 11° C., and the time was adjusted to get the maximum effect with the particular dilutions. Vieille's results are shown in the following table:—

Approximate composition of Acid.	Sp. gr.	Formula of Products.	C.C. of NO yielded per gram.	Remarks.
$HNO_3.\frac{1}{4}H_2O$	1·502 1·497	$C_{24}H_{20}O_{10}(HNO_3)_1$	202·1 197·9	Cotton fibres not detroyed. Product soluble in acetic ether, but not in ether-alcohol.

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* *Compt. Rend.*, pp. 95, 132.

Approximate composition of Acid.	Sp. gr.	Formula of Products.	C.C. of NO yielded per gram.	Remarks.
$HNO_3.\frac{1}{3}H_2O$	1·496	$C_{24}H_{22}O_{11}(HNO_3)_9$ $C_{24}H_{24}O_{12}(HNO_3)_8$	194·4	Cotton fibres still apparently unaffected. Soluble in ether-alcohol. Form collodion cotton.
	1·492		187·3	
	1·490		183·7	
$HNO_3.\frac{1}{2}H_2O$	1·488	$C_{24}H_{26}O_{13}(HNO_3)_7$	165·7	Appearance as before. Soluble in ether-alcohol but solution more gelatinous.
	1·483		164·6	
$HNO_3.\frac{3}{4}H_2O$	1·476	$C_{24}H_{28}O_{14}(HNO_3)_6$	140·5	Cotton dissolved, precipitated by water, gelatinized by acetic ether, not by ether-alcohol.
	1·472		140·0	
	1·469		139·7	
$HNO_3.H_2O$	1·463	$C_{24}H_{30}O_{15}(HNO_3)_5$ $C_{24}H_{32}O_{16}(HNO_3)_4$	128·6	Friable pulp, coloured strongly blue by I in KI. Insoluble in ether-alcohol.
	1·460		122·7	
	1·455		115·9	
	1·450		108·9	

A great advantage is obtained by using a mixture of nitric and sulphuric acids, as recommended by Knop and by Kamarsch and Heeren, and now universally adopted, since by using different strengths of these acids, varying the proportions of the two, and also regulating the time of immersion, any desired result can be obtained up to the highest limits of nitration. The sulphuric acid in this case acts the part of a dehydrating agent, absorbing the water immediately it is liberated, thus maintaining the strength of the nitric acid during the whole time of the reaction.

Cross and Bevan* describe the following cellulose nitrates as well defined:—

Hexanitrate. $C_{12}H_{14}O_4(NO_3)_6$.—Gun-cotton, theoretical percentage of nitrogen 14·14. This is prepared by immersing cotton in a mixture of the strongest nitric acid (sp. gr. 1·5) 3 parts, and sulphuric acid (sp. gr. 1·84)

* *Cellulose*, 1903, p. 39.

1 part, for 24 hours, the temperature not being allowed to rise above 10° C. The proportions of the two acids may, however, be varied considerably, provided they are both concentrated, without appreciably affecting the nature of the product. The hexanitrate is insoluble in ether-alcohol, in methyl-alcohol, and also in acetic acid; but acetone dissolves it, although not readily. This product is extremely explosive, the temperature of ignition being 160° to 170° C. Ordinary gun-cotton usually contains some of the lower nitrates which are soluble in ether-alcohol; this may amount to as much as 10 to 12 per cent.

A. Luck and C. F. Cross,* by treating 1 part of cotton with 60 parts of a mixture consisting of nitric acid 24, sulphuric acid 70, and water 6, obtained a cellulose nitrate containing 13·31 per cent. of nitrogen, 4·3 per cent. of which was soluble in ether-alcohol.

By repeated treatment of cellulose with a mixture of nitric and sulphuric acids, L. Vignon † obtained a final product containing 11 NO groups on the basis of the C_{24} formula, which represents 13·52 per cent of nitrogen.

Pentanitrate. $C_{12}H_{15}O_5(NO_3)_5$.—Theoretical percentage of nitrogen 12·75. This formula has sometimes been applied to gun-cotton, which is no doubt usually a mixture of penta- and hexa-nitrates. By the ordinary methods of nitration it is practically impossible to prepare one nitrate without the other, but the pentanitrate can be obtained in a practically pure state by the method of Eder, due to the discovery of De Vriz, that gun-cotton is soluble in nitric acid at a temperature of 80° to 90° C., and that on cooling to 0°, and adding sulphuric acid a precipitate is formed which has the composition of the pentanitrate. It is freed from acid, etc., by washing with water, and then with alcohol, dissolved in ether-alcohol and re-precipitated by addition of water. The pentanitrate is insoluble in alcohol, but easily soluble in ether-alcohol.

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* *Journ. Soc. Chem. Indt.*, 1900, p. 642.

† *Compt. Rend.*, 1898, p. 1658.

Tetra-nitrate. $C_{12}H_{16}O_6(NO_3)_4$.—Theoretical percentage of nitrogen 11·11.

Tri-nitrate. $C_{12}H_{17}O_7(NO_3)_3$.—Theoretical percentage of nitrogen 9·15.

These two nitrates are formed together when weaker nitric acid is allowed to act on cellulose for a short time only, *i.e.* fifteen to twenty minutes. The product forms "collodion cotton," which is soluble in ether-alcohol, acetic ether, acetic acid, and wood spirit.

Di-nitrate. $C_{12}H_{18}O_8(NO_3)_2$.—Theoretical percentage of nitrogen 6·60. The dinitrate can be prepared by acting upon any of the higher nitrates with warm dilute nitric acid, also by careful treatment with a solution of an alkali.

Generally speaking the higher nitrates or gun-cottons, approximating in composition to the trinitrate, are insoluble in ether-alcohol while the lower nitrates are soluble, that is to say, the solubility of the product varies inversely with the percentage of nitrogen, but this rule does not altogether hold good since the higher nitrates usually contain some portion which is soluble, and, conversely, the lower nitrates contain a portion which is insoluble. Later researches have also shown that by suitable variations in the composition of the mixed acids, and also in the method of treatment, cellulose nitrates may be obtained containing a very high percentage of nitrogen, which are at the same time quite readily soluble in ether-alcohol. The physical condition of the cotton has also a considerable influence upon the composition and properties of the final product.

The appearance of the cotton after nitration is but little affected, but it becomes harsher to the feel, and its tensile strength is considerably reduced. The hygroscopic water is also less (2 to 4 per cent.) than in untreated cotton.

There is a considerable gain in weight by nitration. One hundred parts of dry cotton yielding theoretically 183 parts of the tri-nitrate [$C_6H_7O_2(NO_3)_3$] or 155 parts of the dinitrate [$C_6H_8O_3(NO_3)_2$], actually in the manufacture of gun-cotton about 170 parts of the product are obtained.

The general reactions of the cellulose nitrates, according to Eder, are as follows :—

1. On gently heating with solutions of the alkalies nitric acid is removed in proportion to the concentration.

2. On mixing with concentrated sulphuric acid practically the whole of the nitric acid is expelled.

3. On heating with a mixture of ferrous sulphate and hydrochloric acid the nitrogen is completely liberated as NO.

4. Reducing agents generally, *i. e.* alkaline sulphydrates, ferrous acetate, etc., eliminate the whole of the nitric acid, the product of the reaction being cellulose, is naturally less inflammable.

Reaction No. 3, which is known as Schloesing's method, is applicable to the determination of the nitrogen in gun-cotton, celluloid, etc., and reaction No. 4 is made use of commercially in the "denitration" of artificial silk and celluloid films, both of which will subsequently be referred to.

Action of Acetic Anhydride. Cellulose Acetates.—When cellulose is heated with acetic anhydride in a sealed tube cellulose acetates are produced. With the proportions of 1 part of cellulose to 2 parts of anhydride the mono- and di-acetates are formed, but when the anhydride is in large excess—*i. e.* 6 of anhydride to 1 of cellulose—the triacetate $C_6H_7O_2(C_2H_3O_2)_3$ results (Schönbein). The addition of a small quantity of zinc chloride facilitates this reaction which then takes place at 110–120°.* The product of the reaction was at first believed to be the triacetate, but further examination has shown that under these conditions higher acetates—*i. e.* tetracetate $C_6H_6O(C_2H_3O_2)_4$ or even pentacetate $C_6H_5(C_2H_3O_2)_5$—are formed. Hydrolysis or the addition of OH groups may be assumed to account for this reaction, since the cellulose regenerated from these acetates has become markedly altered in its chemical characteristics. It is probable that the triacetate is the highest derivative of unaltered cellulose.

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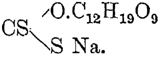
* Cross and Bevan, *Cellulose*, 1903, p. 36.

The lower acetates of cellulose are insoluble in glacial acetic acid in which the triacetate is soluble, forming a very viscous solution. The triacetate is insoluble in water, alcohol, and ether, but dissolves in nitrobenzene on heating; this solution forms a jelly on cooling even when it is very dilute.

Cross and Bevan disclose in their patent (Eng. Pat. 9676, May 17, 1894) a new method of preparing cellulose acetates. The cellulose employed is one of the hydrated forms (cellulose hydrate) which is mixed with a concentrated solution of zinc acetate in the proportion of 1 equivalent of cellulose and 1 to 2 equivalents of zinc acetate. The mixture is dehydrated at 110° C., and subsequently reduced to the state of powder. The dried material is mixed with acetyl chloride in such proportions that 2 equivalents of acetyl chloride are present to 1 equivalent of zinc acetate. The mixture is kept well stirred, and the temperature is not allowed to rise above 30° C. After the reaction is completed the product is thoroughly washed to remove the zinc salts and then dried. The product is dissolved in chloroform in which the cellulose acetate is readily soluble, and the product is filtered to remove any unaltered cellulose or impurities. On evaporation in thin layers the solution dries to a transparent film or sheet of pure acetate.

Cellulose acetate (Acetyl-cellulose) is now manufactured on a large scale, and is used for a variety of purposes. It resembles celluloid, but is non-inflammable.

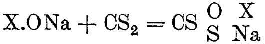
Cellulose Xanthogenate. In 1893 Cross and Bevan announced the discovery of a new derivative of cellulose, which they named cellulose thiocarbonate or Xanthogenate, and to which they ascribe the formula



$$CS\begin{cases} O.C_{12}H_{19}O_9 \\ S\ Na. \end{cases}$$

This product is formed by first treating cellulose (cotton or paper) with caustic soda, and after soaking, so as to form alkali cellulose, stirring in carbon bisulphide. The cellulose then swells up and dissolves to form a thick viscous liquid.

The following equation shows the reaction which takes place:—



$$X.ONa + CS_2 = CS\genfrac{}{}{0pt}{}{O}{S}\genfrac{}{}{0pt}{}{X}{Na}$$

According to the above authors, the proportions most suitable for the reaction are—

$C_6H_{10}O_5$	$2NaHO$	CS_2 *
162	80	76

The most convenient method of preparing this compound is to steep the cotton in a 15 per cent. solution of caustic soda for twenty-four hours, and squeeze out the excess. The cellulose will retain about three times its weight of solution. To this is added in a closed vessel carbon bisulphide, equivalent to about 40 per cent. on the weight of the cellulose, and the mixture is stirred from time to time until the whole is dissolved, whereupon it can be diluted with water as much as may be required.

Cross and Bevan gave to this product the name of "Viscose," and it has come into use very largely, especially in the manufacture of artificial silk. (See p. 103.)

One remarkable property of viscose is that after standing for a time it decomposes spontaneously, forming a gelatinous deposit of cellulose (hydrate), which takes the form of the containing vessel, but smaller, with a yellow liquid consisting of polysulphides surrounding it. Cellulose is at once regenerated from viscose solution on addition of acid.

GUN-COTTON.

The discovery of gun-cotton by Schönbein and Böttger, simultaneously, in 1845, excited general interest, it being

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* Cross and Bevan, *Cellulose*, 1903, p. 25.

then regarded as certain that gun-cotton was destined in time to entirely supersede gunpowder—a supposition that has only recently been to any extent fulfilled. In industries such as celluloid manufacture, where gun-cotton is used, it is made on the spot, owing to the difficulties attending on its conveyance from place to place (though there is little danger when it is transported in a wet state).

Of the numerous methods for preparing this important raw material we will confine ourselves to a description of two of those mostly used at present, namely, those of Lenk and Abel respectively.

Whichever method is used it is of great importance that the nitric acid should be pure (free from chlorine especially) and as strong as possible. The cotton, too, should be thoroughly purified, and the finished gun-cotton freed from acid by treating it with water for several days (this operation formerly took weeks). The slightest trace of residual acid left behind imparts to the gun-cotton a tendency to gradual decomposition, and under certain conditions to easy explosion.

1. *The Lenk Method.*—The cotton is first boiled for two to three minutes in a solution of potash to free it from fatty and resinous substances, and is then drained in a hydro-extractor, washed with water, drained afresh and thoroughly dried. It is next placed in a mixture of one part of nitric acid (sp. gr. 1·48–1·49) and three of sulphuric acid (sp. gr. 1·835), which will convert the cotton into explosive gun-cotton in a few minutes.

The cotton after being taken out and allowed to drain is covered up in stoneware pans for a couple of days to complete the conversion of the cotton as far as possible into pure gun-cotton (hexanitro-cellulose). It is then drained in hydro-extractors, washed with a large volume of water, and laid in running water for three to six weeks. In order to eliminate the final traces of acid, the gun-cotton is boiled with potash solution, followed by draining in the hydro-extractor and washing as before.

2. *The Abel Method.*—In this process cotton-waste

(instead of cotton) is nitrated, the material being freed from fat as in the Lenk method, and treated in an acid mixture of identical composition, in which, however, it is left for twenty-four hours instead of a few minutes. The product is drained in the hydro-extractor, washed quickly in plenty of water and re-drained in the extractor, these operations being several times repeated. The gun-cotton is then passed through a machine similar to that used in breaking down paper stock and treated in a "poaching machine" containing a large quantity of warm water. Owing to the fine state of division obtained by the previous treatment, and to the use of warm water and the poaching machine, the gun-cotton made by the Abel process is completely freed from acid in about two to three days, whereas six to eight weeks are required in the Lenk method.

The resulting loose gun-cotton can be compressed into cylindrical form, but the compressed article is not used in making celluloid.

Properties of Gun-cotton.—Judged merely by appearance, there is no difference between ordinary cotton and gun-cotton, or between ordinary paper and paper that has been treated with the acid mixture, the entire structure in both cases remaining unchanged. The gun-cotton is only a little whiter than the untreated material. If, however, gun-cotton be rubbed, especially at a moderately warm temperature, its fibres become strongly electrified and will adhere to the hand. It also feels somewhat harsher than ordinary cotton, and gives out a slight crackling sound when compressed.

Gun-cotton is exploded by a blow or pressure, but the explosion is restricted to the portion actually affected by the shock, leaving the rest undecomposed. A 56-lb. weight can be dropped on gun-cotton from a height of 40 inches without producing an explosion. The cotton is compressed to about one-third its original dimensions by the blow, and it is only when the weight is dropped from a height of 6 feet that a slight detonation occurs, the bulk of the mass being scattered about by the force generated. Even when the weight is dropped from a height of nearly 40 feet the whole of the gun-cotton will not be exploded, but only a small portion, the rest being dispersed to a considerable distance.

When gun-cotton is heated slowly it begins to decompose at 60° C. with liberation of acid fumes, but, as a rule, no explosion occurs below 130° C. If heated more rapidly it will generally detonate at 150–180° C., often even at 136° C., but rarely below 100° C., though cases have been known where gun-cotton has exploded at 70–100° C. whilst being dried on warm, metal supports. Indeed, in exceptional instances, air at a temperature of 25–30° C. has produced an explosion. Hence great care is necessary in dealing with gun-cotton, especially in the drying process. Many of the explosions occurring at such remarkably low temperatures may have been due to the imperfect elimination of acid; but thanks to the excellent purifying processes of Lenk and Abel, such explosions are now rare.

Wet gun-cotton is much safer to handle than the dry material; and indeed when it contains a sufficient amount of moisture it cannot be considered at all dangerous.

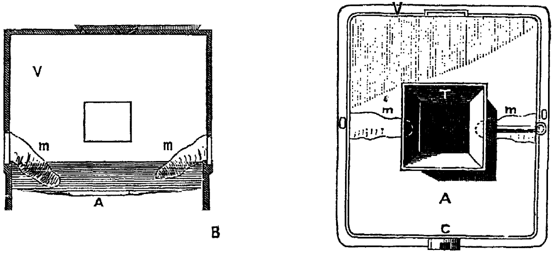
Gun-cotton is insoluble in water, alcohol, ether, chloroform and acetic acid, dilute acids and alkalis; but is soluble in acetone and wood spirit (methyl alcohol).

If saturated with ether, alcohol, carbon disulphide or benzol, gun-cotton decomposes on ignition of the liquid, but without explosion, and an odour of nitrous acid is evolved. Wet gun-cotton is readily ignited by burning dry, compressed gun-cotton. It is soluble in a mixture of drying vegetable oil with half its weight of camphor at about 150° C., to form a plastic mass—xylonite—which can be easily moulded, and furnishes, when dry, a yellowish, semi-translucent mass.

SPECIAL GUN-COTTONS FOR CELLULOID MANUFACTURE.

1. According to the method of B. Tribouillet and L. A. de Besancéle, of Paris, the raw materials (paper,

cotton, linen, hemp or white woods) are dried at 100° C., ground, and then nitrated. This last operation is performed in glass, earthenware or glazed iron vessels, A (Figs. 1 and 2), 7–8 inches deep and mounted on a cooling jacket, B, traversed by a flow of water. Each vessel is surmounted by a glass cover, V, to protect the operator from the fumes. The small hopper, T, in the cover can be closed by a slide, and the lateral opening, C, by a flap.



FIGS. 1 and 2.—Apparatus for making Gun-cotton.

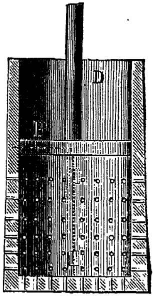


FIG. 3.—Press for Nitro-cellulose.

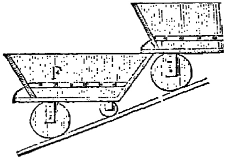


FIG. 4.—
Trucks for Washing Nitro-cellulose.

The ground dry materials are treated in this vessel with an acid mixture left from a previous operation in another vessel. In order to mix the charge, the operator inserts his arms through the opposite openings, *o*, and the attached rubber sleeves, *m*, which cover the arm down to the wrist.

When the mass has been stirred for ten to fifteen minutes with a kind of trowel, it is removed to a press of glazed cast-iron (Fig. 3), with perforated sides and bottom, and is there pressed by forcing down the plunger, P.

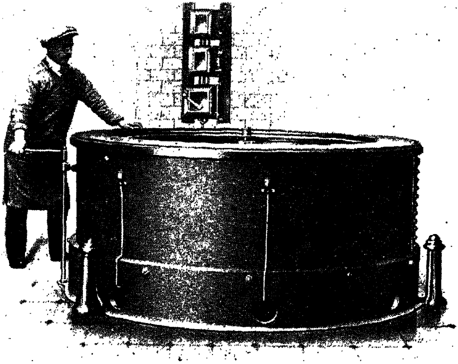


FIG. 5.—Centrifugal Hydro-extractor.
(Thomas Broadbent & Sons, Ltd.)

The resulting cake is next transferred to a second mixing vessel, in which it is treated in a suitable manner with a mixture of three parts of sulphuric acid (sp. gr. 1·834) and two parts of concentrated nitric acid containing nitrous acid in solution, and is afterwards pressed as

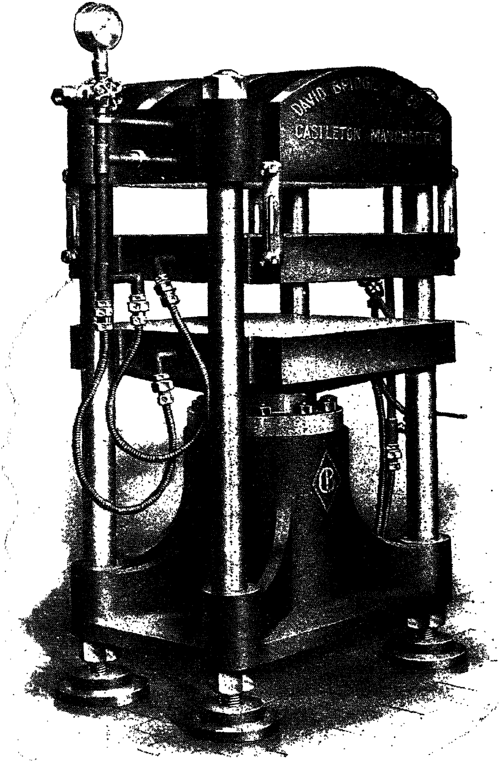
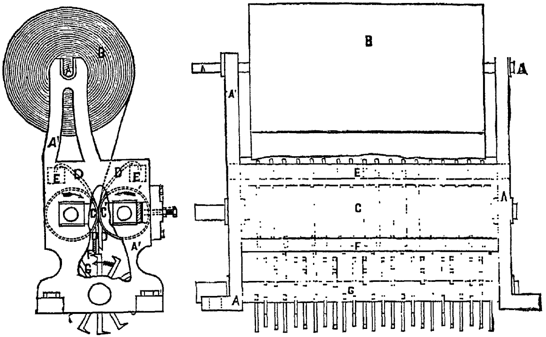


FIG. 6.—Hydraulic Press.
David Bridge & Co., Ltd.)

before. The acid draining from the press is returned to the first mixing vessel, where it is used for a fresh batch of cellulose, after it has been strengthened with concentrated sulphuric acid or dry sodium sulphate.

The pressed nitro-cellulose is next stirred up with water and placed in wooden trucks fitted with false bottoms (Fig. 4). These trucks are mounted on wheels of unequal size, which allows them to be gradually moved up an incline whilst the washing water passes downwards from one to another. The rest of the acid is washed out with water containing a little soda or ammonia, and finally with clean water.



FIGS. 7 and 8.—Machine for Tearing Paper.

The excess of acids may be removed by placing the cotton in a centrifugal hydro-extractor, similar to that shown in Fig. 5, which is made by Thomas Broadbent & Sons, Ltd., Huddersfield. Fig. 6 shows a hydraulic press suitable for pressing out the remainder of the water after the material has been removed from the hydro-extractor. The press is by David Bridge & Co., Ltd., Castleton. The hydro-extractor is also used for removing the water after washing.

2. According to Hyatt, of New York, it is inadvisable to treat paper in unbroken rolls or sheets, since in such case the acid will not penetrate thoroughly; moreover the manipulation of large sheets of paper entails the use of large quantities of acid. He recommends that the paper be torn into fragments as small as possible, and in this condition brought into contact with the acid. The action of the latter is then quicker and more complete while, moreover, a comparatively small vessel can be used.

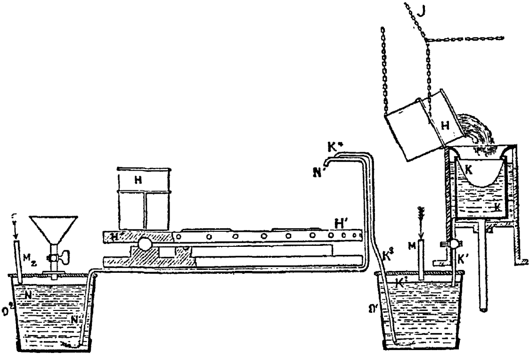


FIG. 9.—Nitrating Plant.

Thin satin paper is employed, and this is torn into small fragments by the apparatus shown in Figs. 7 and 8; Fig. 7 being a side elevation and Fig. 8 a front view. This device consists of one or more rotary rollers, A, on which the paper, B, is wound, the rollers being supported by the bearings, A^1. Only one roller is shown in the illustrations.

From this roller the paper passes to the guide rollers, C, one of which is rotated by friction against the other.

Each of these rollers is provided with a number of circular channels in which rest the guide wires, D, the upper ends of these latter being bent backwards and fastened to the bars, E. They extend below the guide rollers, the one set being attached to knife blades, the cutting edges of which come in contact with the teeth of the rotary breaker, G, so that the paper fed by the rollers, C, is torn into very small fragments.

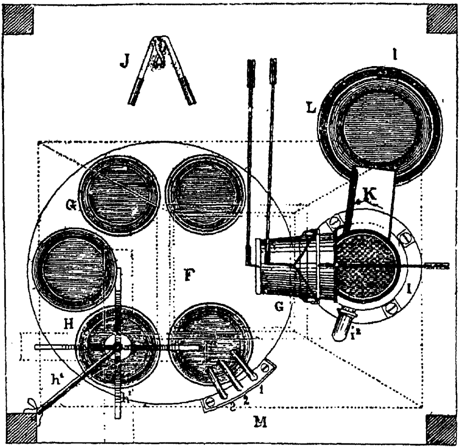


Fig. 10.—A Celluloid Manufacturing Company's Plant.

The rollers are mounted in spring bearings, so that they are always pressed together whether one or more layers of paper be passing through. The paper can be fed to the machine in sheets instead of in rolls.

The fragments of paper are next placed in the vessel, H (Fig. 9), which contains a mixture of sulphuric and nitric acids warmed to about 26° to 32° C. The vessel is provided with a vertical stirrer, I (Fig. 10), which can be rotated rapidly and also lifted up out of the acid and lowered into the same with the minimum of trouble.

This stirrer brings the acid and paper into intimate contact, so that the transformation into nitro-cellulose is quickly effected, which done, the stirrer is removed, and the mass is left at rest for about twenty minutes to complete the operation.

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The vessel, H, is preferably mounted on a turntable, H′, by means of which it can be brought into position under the crane, J (Fig. 9), which lifts the vessel and discharges its contents into the hydro-extractor, K. In this latter all the excess of acid is expelled from the mass, and runs away through the pipe, K′, into the acid tank, O′, whence it is returned to the vessel, H, which at the same time is charged with a proportion of fresh acid from the tank, O^2.

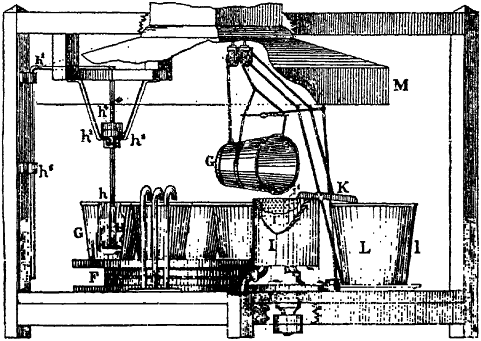


Fig. 11.—Celluloid Manufacturing Company's Plant.

The tanks, O′, O^2, are provided with airtight covers, K^2 and N, which allows the acid to be raised through the pipes, K^2 and N′, into the vessel, H, by compressed air, admitted through the pipes, M′ and M^2.

3. *Methods of the Stains Celluloid Co.*—At this company's works, near Paris, the nitro-cellulose is made by submerging paper, made of cotton and linen and weighing about 1¾ oz. per square yard, for some considerable time in concentrated nitric acid, containing a small proportion of concentrated sulphuric acid, the product being afterwards washed with water as usual.

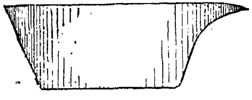
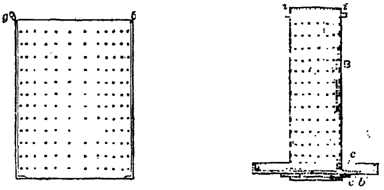


FIG. 12.—Nitrating Vessel.



FIGS. 13 and 14.—White and Schupphous Nitrating Plant.

The following methods of preparing nitro-cellulose are described by Walter D. Field in a paper read before the United States Section of the Society of Chemical Industry. Mixed cotton and flax fibre in the form of paper, from two to three one-thousandths of an inch thick and cut into one-inch squares, is nitrated by the Celluloid Manufacturing Company, and the same paper, left in long strips, one inch wide, is used for nitration by the Zylonite Manufacturing Company. The Celluloid Manufacturing Company introduce the cut paper into the mixed acid by means of the arrangement shown in Fig. 10, H, which is a rapidly revolving hollow tube, flared at the lower end, and immersed in the mixed acid. The centrifugal force of the revolving tube throws the paper towards the sides of the vessel G, leaving the centre of the vessel ready for fresh paper. The Zylonite Manufacturing Company simply cut the paper into long strips and introduce it into the mixed acids by means of forks. The arrangement used by this company for holding the mixed acids was a cylindrical vessel divided into a number of sections, the whole revolving like a turntable, thus allowing the workman to nitrate successively each lot of paper at a given point. This company did not remove the acid from the paper after its immersion, but plunged it immediately into the water, thus losing a large proportion of acid. The Celluloid Company, on the other hand, by using the paper in smaller pieces, using more paper to a pound of acid, and wringing the mixed acid from the paper before immersion, had by much the best process of nitration. Their method of separating the acid and paper will be seen in Figs. 10 and 11.

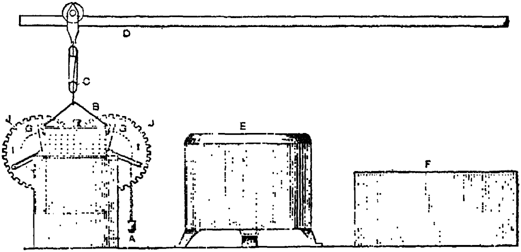


FIG. 15.—White and Schupphous Plant for Nitrating.

The other manufacturers of pyroxylin use earthenware vessels and glass or steel rods, hooked at one end, having small pieces of rubber hose pulled over the other end to prevent the hand from slipping. The form of vessel in general use is that given in Fig. 12. It is sufficient in size to nitrate one pound of cotton. The hook on one end of the rod enables the workman to pull the pyroxylin apart and thus ensures saturation of the fibre.

The nitrating apparatus of White and Schupphous (U.S. P., No. 418,237, 1889) is both novel and excellent in its general plan. The cage B (Fig. 13) with its central perforated cylinder B′ (Fig. 14) is intended to ensure the rapid and perfect saturation of the tissue paper used for nitrating. The patentees say that no stirring is required with their apparatus. This might be true when paper is used, or even cotton, when the temperature of nitration is from 30° to 35° C., but would not be true if the temperature were raised to 50° or 55° C. In carrying out their process they proceed as follows: The paper is nitrated in the cage B, the bottom of which is formed by the flanged plate *c* fastened to the bottom of the internal cylinder B′. After nitration the cage is carried to the wringer E, Fig. 15, of which it forms the basket, and the acids removed. Finally the cage is taken to the plunge tank F, where the paper is removed from the cage by simply pulling out the central perforated cylinder B′. Fig. 16 shows the nitrating pot, with its automatic cover.

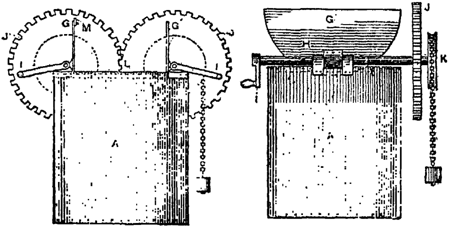


FIG. 16.—White and Schupphous Plant for Nitrating.

NITRATING CENTRIFUGALIZERS.

These machines, mainly intended to expel from the interstices of the cotton the air which hinders nitration,

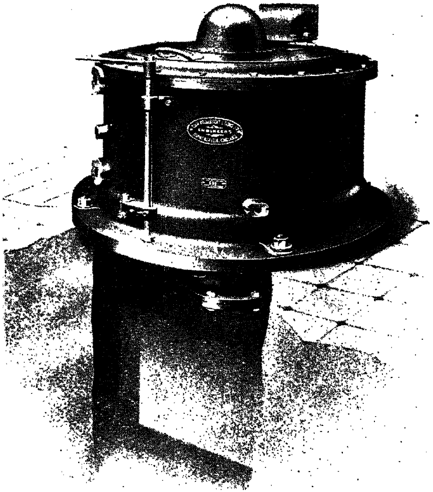


FIG. 17.—Electrically Driven Nitrating Centrifugal.
(Thomas Broadbent & Sons, Ltd.)

are made in different patterns. These have certain advantages over the ordinary nitration pots, especially when large quantities of cotton have to be dealt with, but it is necessary to have them lined with material which is unaffected by the acids and the fumes evolved. The capital outlay and the working costs are of course greater, but this is offset by the greater facility of working and the ease with which the acid is removed after nitration is completed. Fig. 17 shows an electrically driven nitrating centrifugal, made by Thomas Broadbent & Sons, Ltd., Huddersfield, and Fig. 18 a section of a similar machine of Selmar and Lange, consisting of a hydro-extractor of the ordinary type, fitted with a perforated iron cage, B, 33 inches in diameter, inside the casing, A. The lid is fitted with a hinged cover, C, for the introduction of the cotton. It is also provided with an 8-inch exhaust pipe for carrying away the acid fumes, which are drawn off in the ordinary manner, by means

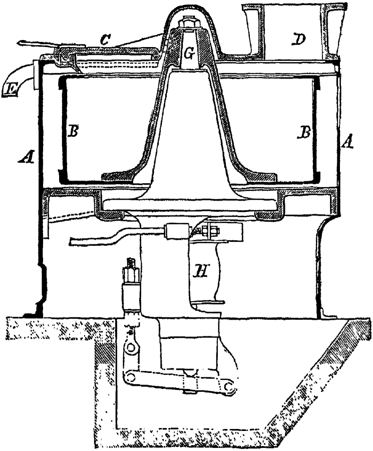


FIG. 18.—Section of Nitrating Centrifugal.

of a fan, and delivered through earthenware pipes to an absorption tower. The cage is suspended, in the usual manner, by means of a collar-bearing, G, and is revolved by a belt pulley, H, mounted on the lower extension of the central shaft. A hand brake, I, brings the machine quickly to a standstill when the process is ended. To work the machine, the acid draw-off tap in the bottom of the casing is closed, and the acid is run in until the vessel is filled to within about an inch from the top. The machine is set running at low speed, and about 17 lb. of cotton is entered by degrees, which raises the level of the acid to within half an inch of the top. The machine is then left to itself, with the lid open, there being no objection to this, as the exhaust fan prevents any escape of acid fumes.

In about twenty minutes the operation is completed, whereupon the acid is drawn off, the lid closed, and the machine set to run at high speed, thus removing the remaining excess of acid, which done, the cotton is taken out with a pair of tongs. The advantage of nitrating with this apparatus is that the expelled acid can be easily collected and used again. The apparatus also enables large quantities of material to be treated at each operation.

Collodion Cotton.

This substance differs from gun-cotton by being almost non-explosive, and by its solubility in a mixture of alcohol and ether, in which gun-cotton is insoluble. The method of preparation also differs, inasmuch as a highly concentrated nitric acid and a low temperature are employed for gun-cotton, whereas in the preparation of collodion wool a rather more dilute nitric acid is used, or this acid is replaced by a mixture of nitric and hydrochloric acids. Frequently also a comparatively high temperature (50–70° C.) is employed, a weak acid and a warm bath favouring the production of collodion pyroxylin.

The collodion cotton more particularly used for photographic purposes and the manufacture of celluloid, etc., consists mainly of tetranitro-cellulose, mixed with trinitro-cellulose. Owing to the conditions of formation of pentanitro-cellulose and dinitro-cellulose, these substances, which also constitute collodion cottons soluble in ether-alcohol, are not formed to any extent, if at all, by the method of preparation of true collodion cotton.

METHODS OF PREPARING COLLODION COTTON.

1. One part, by weight, of cotton is immersed in a mixture of 20 parts of sulphuric acid and 9 of powdered saltpetre, in which it is left until a small sample, after a quick washing with water, squeezing, suffusing with alcohol and squeezing again, is found to dissolve rapidly and completely in a mixture of 2 parts of ether and 1 of alcohol. When this result is attained, the collodion cotton is washed thoroughly with water, pressed between linen, and left for twenty-four hours in contact with alcohol, which dissolves a small proportion, acquiring a yellow tinge. The collodion cotton is next pressed again and immediately dissolved in 2 parts of 90 per cent. alcohol and 10–20 parts of ether (sp. gr. 0·73).

2. Pure cotton, freed from fat by boiling with a solution of sodium potassium carbonate, is placed in a mixture of 7 parts of nitric acid (sp. gr. 1·43) and 9 of pure sulphuric acid, at a temperature of 54–58° C. for five to eight minutes, after which it is squeezed and washed.

3. One part of cotton is left for twelve to twenty-four hours at ordinary temperature in a mixture of 7 parts of nitric acid (sp. gr. 1·42) and 9 of sulphuric acid (sp. gr. 1·833), or 8 parts of nitric acid (sp. gr. 1·39) and 20 of sulphuric acid. The collodion cotton thus produced is then squeezed and washed.

4. One to $1\frac{1}{2}$ parts of cotton are immersed in a mixture of 20 parts of nitric acid and 30 of sulphuric acid, cooled to 50° C., left therein for twenty-four hours and then washed.

5. To prepare collodion cotton from pure satin paper, the latter is steeped in a mixture of 275 parts of nitric

acid (sp. gr. 1·47), 275 parts of sulphuric acid (sp. gr. 1·84) and 75 of water. An alternative mixture is one of 50 parts of the same nitric acid, 100 of nitric acid (sp. gr. 1·36), and 100 of sulphuric acid (sp. gr. 1·84). Eighteen parts of the paper are left in the solution for an hour at 55° C., during which process it increases about 40 per cent. in weight. It is then washed with water.

6. Schering's collodion cotton consists chiefly of tetra-nitro-cellulose. It has already been mentioned that a collodion cotton of analogous composition can be obtained by treating cotton for fifteen minutes at 80° C. with a mixture of equal parts of nitric acid (sp. gr. 1·40) and sulphuric acid (sp. gr. 1·845).

7. Celloidin cotton is the purest collodion cotton, free from all organic impurities capable of entering into combination with nitric acid, such, for instance, as dextrin, xyloidin, nitro-mannitol, etc.

Celloidin is prepared by dissolving collodion cotton in ether-alcohol, precipitating it with water, drying, re-dissolving and then filtering through a special filtering apparatus. The solution is precipitated again, and the precipitate re-dissolved in a mixture of ether and alcohol, and filtered as before.

The clear filtered collodion is freed from ether and alcohol by distillation to such an extent that the highly viscous residual mass can be poured into moulds while still warm. The gelatinous, glue-like mass obtained on cooling is cut up into lumps, each of which contains a definite weight of pure, dry collodion.

This celloidin is neither inflammable nor explosive. On ignition it burns like paper, without exploding; heated in a test tube it slowly carbonises. It is used almost exclusively for photographic purposes.

MOWBRAY'S METHOD OF PREPARING NITRO-CELLULOSE OR PYROXYLIN.

The conversion of the raw material into nitro-cellulose is generally attended with numerous manipulations, requiring the constant care of a large number of skilled workmen, thus entailing very high cost of production.

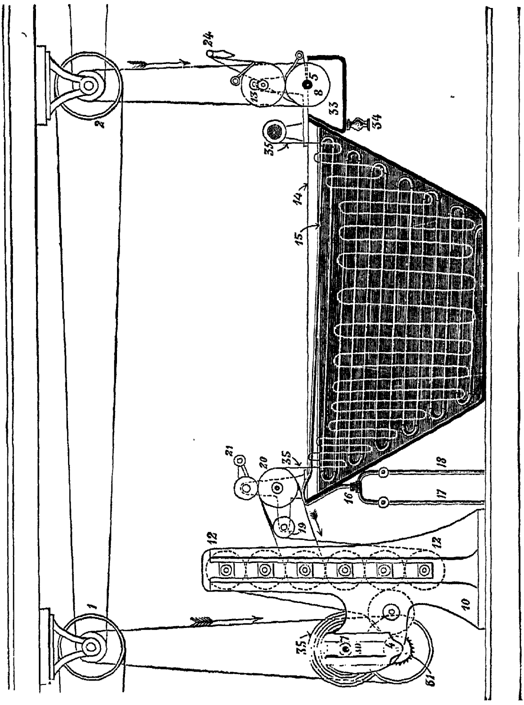


FIG. 19.—Mowbray's Plant for Nitrating.

For this reason it is highly advantageous to meet with a process, such as this, by means of which, with a smaller staff and less supervision, a far cheaper and superior product, ready for further use, can be continuously obtained from a roll of cellulose paper. The principal new features of this process consist:—

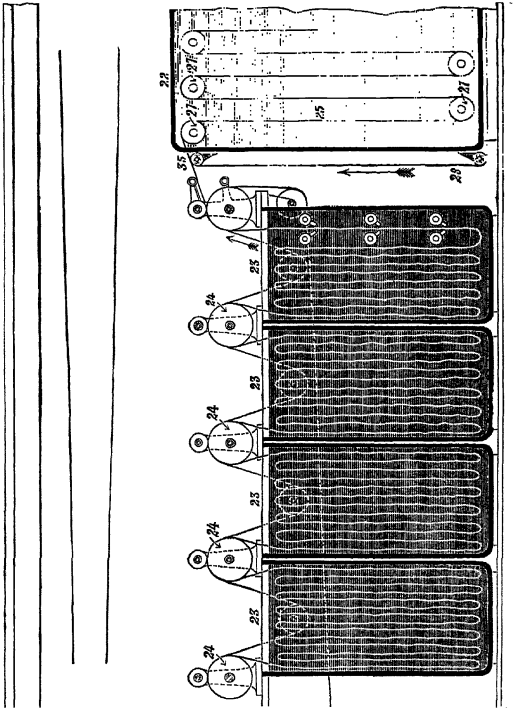


FIG. 20.—Mowbray's Plant for Nitrating.

1. In passing the unsized cellulose paper through a warm calender, and feeding it direct into and through an acid bath.

2. In feeding a continuous band of cellulose paper into an acid bath at the same time as the immersed and nitrated portion is being withdrawn.

3. In pressing the nitrated paper after leaving the bath, feeding this pressed, nitrated continuous band

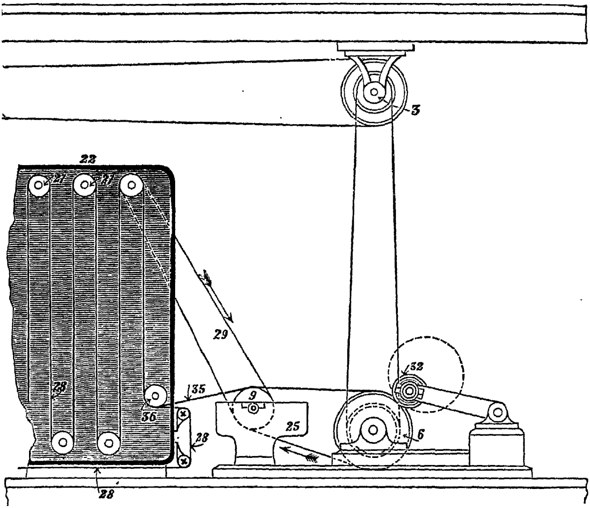


FIG. 21.—Mowbray's Plant for Nitrating.

through a washing liquid and a drying apparatus, distributing a solvent on the moving band, and rolling the latter up.

The various parts of the apparatus are shown in section in Figs. 19–21, whilst Fig. 22 shows a general view of the whole, and Fig. 23 represents a modification of the device for applying the solvent.

The frame, 10 (Fig. 19), which supports both the shaft, 4, and the roll of paper, 7, is fitted with a number of superimposed hollow drying cylinders, which are heated by steam or hot water. Between the frame, 10, and the pressure rollers, 8 and 13, is a tank containing the suitably compounded mixture of nitric and sulphuric acids for converting the continuous bands of cellulose into nitro-cellulose or pyroxylin. The acid tank contains a pipe, 15, connected with a steam pipe, 17, and a water pipe, 18, by means of a T-piece, 16, for the purpose of enabling the temperature of the bath to be adjusted when necessary. A feed roller, 19, and carrier roller, 20, with a wiper, 21, are mounted near the pressure rollers at the feed end of the tank. Between the pressure rollers and the drying chamber, 22 (Fig. 22), are a number of superimposed washing tanks, 23, filled with water, each of which is fitted with a carrier roller, 24. The latter are rotated in the proper direction by a suitable device driven from the shaft, 5, of the pressure roller, or in any other similar way. These carrier rollers are preferably covered with an acid-proof coating, or shod with rubber.

Between the drying chamber, 22, and the roller, 6 (Fig. 21), is a vat, 25, containing a solvent liquid, which is applied to or distributed on the moving bands by means of the rotary smooth or channelled distributing cylinder, 9.

The solvent liquid may consist of camphor dissolved in alcohol; but no mention is made of any special solvent or of the means for re-winding the paper bands, since various means for these purposes are available.

If desired, suitable dyes may be mixed with the solution, either by dissolving them therein, or adding them ready dissolved.

Passing over the rollers, 27, mounted at the top and bottom of the drying chamber, is an endless belt, 28, by means of which the band of paper is carried through the drying chamber. This belt, 28, is kept in constant motion in any suitable way, such as a belt, 29, driving one of the rollers from the intermediate pulley, 9, which in turn is driven from the shaft, 6, by a belt or other means.

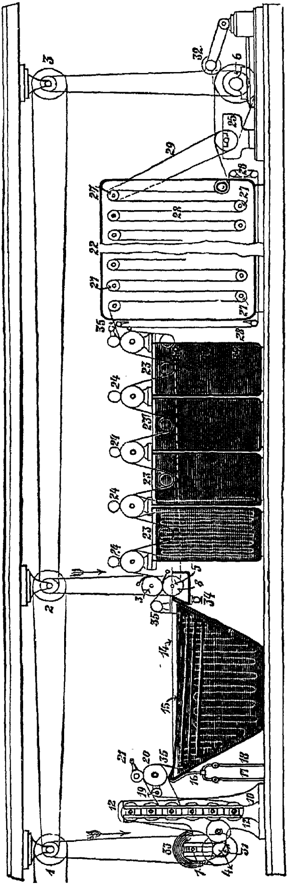


FIG. 22.—Mowbray's Plant for Nitrating.

The shaft, 7, is mounted in bearings which slide up and down in vertical slits on the frame, 10, immediately above the drying shaft, 4.

The cylinder, 31 (Fig. 19), mounted in this manner, carries a perforating device of needle points or the like for the purpose of perforating the cellulose paper while on its way to the acid bath, so as to increase the surface and facilitate the penetration of the acid. The winding cylinder, 32 (Fig. 21), mounted at the end of the machine, for rolling up the band of paper, may be hollow, and mounted in such a manner as to receive motion from the roller, 6, by friction. The pressure rollers, 8 and 13, are situated above a tank, 33, which collects the acid expressed by these rollers, which acid is then returned through pipes, 34, to the acid tank.

The shafts, 5 and 6, are driven by belting from the driving pulleys of the overhead shafting, 1, 2 and 3.

The unsized cellulose paper rolled on the hollow shaft, 7, is drawn upward by the rotary perforator, 31, which penetrates through one or more layers of the fine paper. The latter passes to the topmost drying cylinder, 12, and thence downward between the others in succession until the bottom is reached, from whence it goes over the rollers, 19 and 20, and under the wiper, 21, to the acid tank, 14.

In starting the apparatus, two men—one on either side of the tank—guide the paper from the rollers, 19 and 20, to the farther end of the tank, passing the paper up and down in the positions indicated by the lines in the drawing, this being necessary to prevent the paper from becoming entangled. The paper remains ten to twenty minutes in the acid bath, for nitration, and then, while the next following length of paper is being immersed, the portion already in the bath is withdrawn. This operation takes nearly as long as the immersion. On issuing from the acid bath the nitrated paper passes over a guide roller to the pressure rollers, 8 and 13, which squeeze out the superfluous acid, which, as already mentioned, is collected in the tank, 33, and is run off through a pipe, 34, to the acid tank or an empty tank.

The nitrated paper is next passed over the first roller, 24, through the first water tank, 23, and so on, the superfluous water being removed by the wiper. On leaving the last water tank the paper is fed to the endless belt, 28, which conveys it round the rollers, 27, through the drying chamber, 22.

To hasten the drying process the nitrated paper, before entering the well-ventilated drying chamber, is brought into contact with an absorbent material which takes up the liquid remaining on the surface.

The endless belt, which leaves the paper band at the rollers, 36, passes back, outside the drying chamber, to its starting-point, to resume its functions until the entire roll of paper has run off. The washed nitrated paper passes over the cylinder, 9, that dips into the solution bath and transfers a suitable amount of the solution to the paper by means of its smooth or channelled surface. This done, and after the nitrated paper has been thoroughly permeated by the solution, it is wound on the hollow cylinder, 32. Instead of using a distributing cylinder, the nitrated paper may be passed through a tank in which it is thoroughly steeped with solution. The rate at which the paper is moved is under the control of the overseer, who can regulate the speed of the motor or the driving shafts by suitable means, and thus increase or lessen the time the paper is left in the acid bath. Two rollers, 37 (Fig. 23), one in front and the other behind the distributing cylinder, are mounted on arms, 38, which can be raised or lowered by means of screws, 39. By this means the

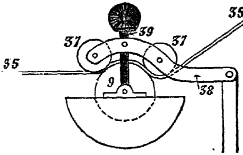


FIG. 23.—Mowbray's Plant.

rollers, 37, are adjusted with reference to the surface of the cylinder, 9, thus pressing the nitrated paper with more or less force against the cylinder.

According to H. Jentgen,* in using nitric acid alone for the preparation of xyloidins, the strength of acids most suitable at 18° C. range between the specific gravities 1·469 and 1·479; and to obtain homogeneous products it is essential that the cellulose should dissolve almost entirely in the liquid, being precipitated as the nitrate on dilution. A method which he recommends is to moisten 10 parts of loose cotton with twice its weight of water and then immerse it in 300 parts of nitric acid, sp. gr. 1·5, until dissolved, cooling if necessary. The preparations produced in this way contain from 6·2 to 8·8 per cent. of nitrogen, according to the strength of acid and the conditions of the treatment. The products containing 6 to 7 per cent. of nitrogen are insoluble in all the ordinary solvents employed for nitro-cellulose, and those with the higher percentages are soluble. The xyloidins contain 2·5 to 4 per cent. of hygroscopic moisture, and ignite at a temperature of 196° to 197° C.

Nitro-cellulose made from unbleached cotton must be bleached before it can be used. This is done by disintegrating the pyroxylin and treating it first with a weak solution of carbonate of soda and then with water. The washed material is passed into large truncated vats provided with agitating gear capable of holding about 2200 gals. of liquid. In these vats the material is treated with a solution containing 2 per cent. of potassium permanganate in which it is kept moving for about half an hour. At the expiration of this time a strong brine of common salt is added and a sufficiency of hydrochloric acid to decompose all the permanganate, the bleaching being complete in about an hour. The nitro-cellulose is first washed with water, steeped in dilute sulphuric acid, again washed with water, put through the centrifugal machine to remove excess water, and then further partially and carefully dried till it contains about 40 per cent. of water, when it is ready for conversion into celluloid.

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* *Z. angew. Chem.*, 1912, 944. See also T. C. Haussermann, *Z. angew. Chem.*, 1910, 1761.

D. Spill took out a patent (Eng. Pat. No. 180, 1870) for thus bleaching xylonite or soluble gun-cotton by using a solution of chloride of lime, chlorine, sulphurous acid, a soluble sulphite, or other bleaching agent.

CHAPTER II

OTHER RAW MATERIALS

CAMPHOR

FORMERLY the term "camphor" was a generic name for the crystalline deposits which separate from ethereal oils, or for certain volatile substances recovered from various vegetable or animal substances; hence the names bergamot camphor, tonka camphor, cantharides camphor, etc. At present, however, the name is restricted to a well-defined substance which is distinguished by a peculiar smell and by other characteristic properties. There are several other products, sometimes known as camphols, resembling ordinary camphor more or less, such as Borneo camphor, or Borneol, $C_{10}H_{17}OH$, in addition to which may be mentioned blumea camphor, rosemary-oil camphor, matricaria camphor, lavender-oil camphor, patchouli camphor, cubeb camphor, cedar camphor, cypress camphor, ledum camphor, ylang-lang camphor, and menthene camphor, or menthol, $C_{10}H_{19}OH$, from oil of peppermint.

Recently, artificial camphor has been prepared by synthetical processes.

JAPANESE (FORMOSA) CAMPHOR, ORDINARY CAMPHOR, $C_{10}H_{16}O$.

This camphor is furnished by the bark, wood, and to a smaller extent by the flowers and leaves, of *Laurus* (*Cinnamomum*) *camphora*, a large tree of the Order Laurineæ, indigenous in China and Japan, where it forms whole woods in some places. On splitting the wood the camphor is found to some extent in the crevices in the form of "tears" or "crystals"; and as much as 22 lb. is said to have been obtained in this form from one tree. The camphor tree, which thrives best in a mild, damp atmosphere, is widely distributed throughout Japan, occurring in all three of the chief islands, Nippon, Kinhin, and Sikok. It thrives best, however, in the south, especially in the provinces of Tosa and Sikok, where the chief centres of production of camphor are situated.

The extraction of camphor, as practised in Japan and Formosa, is a very primitive process, the wood and branches being chopped small and boiled with water in iron pans, covered over with earthenware pots or hoods filled with rice straw or dry brushwood. Camphor and ethereal oils are liberated with the steam, the camphor condensing on the rice straw or twigs in the form of a grey, granular mass. This mass, which is highly impregnated with camphor oil, is separated from the twigs or straw as far as possible, and then left for the bulk of the camphor oil to drain away, the product being placed on the market as crude camphor.

Dr. A. von Koretz reports on the recovery of camphor as follows: As soon as a suitable spot has been found in the vicinity of a few camphor-trees, the camphor-seekers erect a camp and a furnace for preparing the crude camphor; when the supply is exhausted, the camp is broken up and a move is made to another site.

The selected camphor-tree is felled, chopped into small, regular chips with a hollow-ground, short-handled chopper, the roots are also dug up and chopped small, the whole being packed into baskets and carried to the furnace. The latter is usually erected on sloping ground, near to running water, and is worked as a wet still.

A small ring of stones, *a*, serving as a hearth (Fig. 24), is surmounted by a shallow iron pan, F, about 25 inches diameter. This in turn supports a perforated cover, E, which is luted on with clay, and which also serves as the bottom of a barrel, B, about 40 inches high and 18 inches in diameter at the top. A square opening, D, is provided near the bottom of the barrel, which is closed by a tight-fitting board. The whole is surrounded with a thick layer of loam, C, held together by bamboo hoops. The opening at the top is covered with a luted lid, G, containing an aperture closed by a plug, K.

Just under this lid is a bamboo pipe, L, leading to the condenser, H, which is a rectangular box, open below, and divided into five communicating divisions by partitions. This condenser is fitted into a water tank, and is kept cool by running water over the top.

The lid, G, being removed, the chips are placed in the barrel, B, the lid is then replaced and luted on with clay, and a small quantity of water is poured in through the hole, K, on to the chips, through which it trickles down into the pan, F.

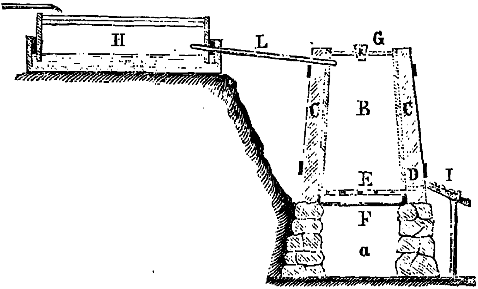

FIG. 24.—Distillation of Camphor.

Heat is now gradually applied, the water in F being boiled gently with a slow fire for about twelve hours; the steam ascending through the chips extracts all the camphor and volatile oils, which are deposited on the surface of the water in the condenser, H. At the end of twelve hours the chips are taken out through the opening, D, the apparatus is cleaned, and the camphor collected in H is packed into barrels. A slight pressure applied to the camphor in these barrels suffices to express about 25 per cent. of a water-white oil, a further quantity escaping through the staves when additional pressure is applied. The fairly dry product is generally sent to Osaka, which is the chief emporium for camphor.

None of the camphor exported has been thoroughly purified, the Japanese article being always freed from the still adhering oil by distillation after its arrival in Europe.

There are two kinds of crude camphor, one being the highly esteemed Japanese or Dutch crude, which usually comes on the market in cylindrical form, with plaited straw wrappers, the packages weighing 1–1$\frac{3}{4}$ cwt. The second kind is the Chinese crude camphor, which comes from Formosa *viâ* Canton and Bombay, and is packed in lead-lined boxes containing $\frac{1}{2}$–1$\frac{3}{4}$ cwt.

In Europe, and more particularly in England, Holland, France and Germany, the crude camphor is purified by sublimation, for which purpose it is mixed with a little lime, iron filings or ashes, and placed in broad, low, wide-necked, flat-bottomed glass flasks, which are filled about half full and placed on a sand bath, numbers of these flasks being used at each operation. The temperature is rapidly raised to about 120° C., and when all the moisture has been expelled, the heat is very gradually increased to 190–200° C. At this temperature the camphor sublimes, and collects in the neck of the flask in the form of a dense, coherent, crystalline mass; camphor oil, which has latterly been used as a substitute for oil of turpentine, being recovered as a by-product.

The refined camphor is in the form of concavo-convex cakes or loaves, with a central hole corresponding to the orifice of the sublimation flask. The weight of the loaves varies between 2 and 11 lb. The flasks have to be broken in order to remove these cakes.

American camphor is very dense, and therefore less easily volatile, owing to its having been pressed into cakes, under heavy pressure, after sublimation.

BORNEO CAMPHOR (BORNEOL, SUMATRA CAMPHOR, CAMPHOL, BAROS CAMPHOR), $C_{10}H_{17}.OH$.

This product is obtained from *Dryobalanops camphora*, which is indigenous in Sumatra, Borneo and Java. It collects in cavities in the old tree stems, but is also stated to collect when cavities are made in young ones. The trees die quickly after this operation, and the hollows are then found to be more or less encrusted with Borneo camphor.

This camphor occurs in small, colourless, transparent, pulverulent crystalline fragments, which seldom unite to form large lumps. It is white, translucent to transparent, and rather brittle; the smell resembles that of camphor, with a little of pepper also, and the taste is sharp and biting.

Borneo camphor melts at 206° C. and boils at 212° C., both these figures being higher than those of ordinary camphor. It is lighter than water, in which it dissolves with difficulty, is readily soluble in alcohol and ether, the alcoholic solution showing a rotation of $[\alpha]_D = +33°$, and when heated with nitric acid is converted into ordinary Japanese camphor, a property of which use might be made if this variety were put on the European market in larger quantity.

PROPERTIES OF CAMPHOR.

Pure camphor melts at 175° C. and boils at 204°, but it sublimes even at the ordinary temperature, as shown by the deposition of crystals on the sides of ordinary closed vessels in which camphor has been stored for a time. It crystallizes in the hexagonal form, and when the crystals are allowed free development, as hexagonal tables. It is readily soluble in concentrated acetic acid, but almost entirely insoluble in water, one part of camphor requiring over 1000 parts of water for its solution (1300 parts at 20° C.). The alcoholic solution has a strong dextro-rotatory effect on the plane of polarized light.

Specific rotation $[\alpha]_D = 55{\cdot}4°$. The crystals exhibit double refraction, but no rotatory polarization. At 12° C. the sp. gr. is 0·995, but at 6° C. and below, the density is almost exactly that of water, so that camphor crystals scarcely sink at all in very cold water. A more remarkable property of pure camphor is that of spontaneous motion which it exhibits when placed on the surface of water, whereas if contaminated with camphor oil or other impurities it usually no longer exhibits this property. In an unaltered state camphor is pulverizable with difficulty, but becomes pulverulent when moistened with alcohol or other solvents. Pure camphor has an aromatic, rather bitter taste, somewhat heating at first, but afterwards cooling. It is readily inflammable and burns with a smoky flame.

According to reliable reports and certain observations made by Prof. Wiesner, no adulterations have yet been practised with camphor.

Camphor possesses a peculiar action on collodion cotton and gun-cotton, in the first named reducing its tendency to inflammability, and in the second adding considerably to its stability, a property which is utilized in the manufacture of explosives.

Nobel found that a special kind of collodion wool dissolves completely in nitro-glycerine, furnishing therewith a gelatinous or gummy substance which contains no inert material and is therefore much more powerful than kieselguhr dynamite. By the addition of certain substances (acetone, benzol, nitro-benzol) that are soluble in nitro-glycerine, it was found possible to render the new explosive highly insensitive to the chemical impulses which induce explosion, without unduly affecting the power of the explosion itself.

Trauzl pursued the matter further and found that the addition of a very small proportion of camphor (which is exceedingly soluble in nitro-glycerine) furnished an explosive that is much less sensitive to mechanical influences, and especially to shots fired even at a short distance away.

The stabilizing action of camphor on blasting gelatine is really remarkable. When 10 per cent. of camphor is added the blazing gelatine can no longer be made to explode by gradual heating, the mass merely scintillating slowly. When heat is applied rapidly the explosion temperature is too high to be accurately measured with the appliances hitherto available.

This remarkable property of camphor to reduce the explosibility of the two most powerful explosives, nitroglycerine and gun-cotton, is also exercised in the case of celluloid, the explosibility of collodion cotton being entirely prevented by incorporating camphor with it. At present, however, the *modus operandi* of the camphor, and the nature of the combination between camphor and collodion, from which celluloid is formed, remains in complete obscurity.

ARTIFICIAL CAMPHOR.

The raw material for the production of artificial camphor is oil of turpentine, or other terpene oils, the process of the Ampère Electro-chemical Co., of Jersey City (N. J.), for example, being based on the action of compounds (such as oxalic acid), capable of introducing CO,OH groups into the molecule of turpentine in such a manner as to form ethereal derivatives which can be converted into camphor by suitable oxidation. Five parts, for instance, of anhydrous turpentine are mixed with one of anhydrous oxalic acid, and the mixture is heated to temperatures below the boiling-point of turpentine, *i. e.* below 120–130° C. A reaction occurs between the oxalic acid and the turpentine, a mixture of camphor and borneol being formed. These products are separated from any accompanying by-products by the aid of steam, and oxidized with potassium bichromate and sulphuric acid to convert the borneol into camphor, the change being effected by the introduction of one molecule of oxygen and the elimination of one molecule of water. Borneol itself is formed from turpentine and formic acid. According to the method of the Porchester Chemical Co., of New

York, artificial camphor is obtained by allowing oil of turpentine to act on oxalic acid at a suitable temperature, the mixture being then treated with lime, the resulting camphor and borneol being distilled off and the latter oxidized to camphor. According to Woods (London), terebin monohydrochloride, prepared by acting on American turpentine with hydrochloric acid gas, or by sublimation in a current of steam, is converted into solid camphene by boiling it with sodium acetate and a caustic alkali or carbonate. The camphene is oxidized into camphor by heating with an alkali permanganate, chromate, bichromate, ferrate, or chlorate, and very dilute sulphuric acid. Camphor can also be prepared from camphoric acid (obtained from American oil of turpentine) by reduction with nascent hydrogen and boiling with camphene in presence of sodium acetate or formate.

CAMPHOR SUBSTITUTES.

A number of substances have been proposed as substitutes for camphor, owing to its high price and pungent smell, but up to the present none of these can be regarded as perfectly suitable. Among those proposed for this purpose, especially in the manufacture of celluloid, may be mentioned: naphthalene, naphthyl acetate, phenoloxylacetic acid, naphtholoxylacetic acid, with their anhydrides and esters, methylnaphthylketone, dinaphthylketone, methyloxynaphthylketone, dioxynaphthylketone, and derivatives of aromatic sulpho-acids of the general formula RSO_2A, in which R represents an acid radicle or a substitution product of the same, and A either an aliphatic (or aromatic) ether radicle, or a singly or doubly substituted amido group. Others are: neutral phthalic acid, alkyl or alphyl esters, esters of the oxamine and oxanil acids, inorganic esters of phenol and naphthol (especially with phosphoric acid, *e.g.* triphenyl phosphate), halogen-substituted aromatic hydrocarbons, both mono- and poly-substitution products, such as dichlorobenzol, etc., acetyl derivatives of secondary aromatic amines (*e. g.* acetyl diphenylamine, acetyl phenyltolylamine, etc.), carbonates of phenols, cresols or naphthols, acid or neutral esters of sebacic acid, thio derivatives of the phenol esters (*e. g.* triphenylthiophosphate), organic esters of sugars (*e. g.* glucose dibutyrate, lactose, tartaric acid, saccharose acetate, etc), cellulose acetate, nitro products from the distillation of petroleum and mineral oils, acetochlorhydrins, acetines, benzicines, esters of phthalic acid or its anhydride, or esters of succinic acid and aliphatic alcohols, etc., α and β phenylnaphthalene, α and β benzylnaphthalene, α and β dinaphthyl, α and β dinaphthylmethane, phenol-alcohol esters of phosphoric acid and halogen-substitution products of same, halogen-substitution products of triphenyl, tricresyl and trinaphthyl phosphates, diphenylcresol phosphoranilide, alkyl and alphyl esters of aromatic sulpho-acids, nitronaphthalene, phthalic anhydride, phthalonic acid, benzoltricarbonic acid and esters of these compounds, acetyldiphenylamine, triphenyl phosphate, amylidene dimethyl and diacetyl ether, and formylated albumin.

The following patents relate to the use of camphor substitutes in the preparation of celluloid:—

J. Schmerber (French Pat. 340,266, 1904) claims the use of methylacetanilide as a substitute either for the partial or entire replacement of camphor, and states that 40 parts of the two materials or 30 to 35 parts of methylacetanilide, together with the usual quantity of alcohol, have an effect on 100 parts of nitro-cellulose equal to that of 50 parts of camphor.

In 1905 A. Behál took out a patent (Eng. Pat. 11,512, 1905) for the use of borneol in place of camphor, the product consisting almost entirely of isoborneol produced by the hydration of camphene being particularly applicable for the purpose. As an example, 1 kilo of nitro-cellulose is moistened with alcohol of 96 per cent. strength and is then incorporated with a solution of 500 grams of borneol in 500 to 600 grams of ethyl acetate. The excess of solvent is removed in a centrifugal machine or by any other suitable means, the celluloid being then worked up in the usual manner. If desired camphor may also be employed.

A similar claim is made by J. Basler and Co. (Ger. Pat. 185,808, 1905) for the use of borneol, dissolved in a solvent for nitro-cellulose, in partial or entire replacement of camphor.

Act. Ges. f. Anilinfabr. (Ger. Pat. 180,208, 1905) have patented the use of symmetrical methylbenzoyltrichloranilide in the manufacture of celluloid, the proportions being 30 parts of the compound mixed with 100 parts of nitro-cellulose mixed with alcohol. In a later patent (Ger. Pat. 180,126, 1906) certain ortho-diamines are to be used in place of camphor, for example, 30 parts of methenyl-*o*-toluylene diamine (melting point 113°–115° C.) are mixed with 65 parts of nitro-cellulose and 70 parts of alcohol.

In the patent taken out by C. Claessen (French Pat. 364,604, 1906) it is stated that camphor may be partially or entirely replaced by compounds belonging to the group of tetra-substituted ureas in which all the hydrogen atoms of the amino group are replaced by organic radicles.

O. B. Thieme's patent (U.S. Pat. 831,488, 1896) also relates to the use as camphor substitutes of ureas in which the hydrogen associated with the nitrogen is replaced by organic radicles.

Badische Anilin und Soda Fabrik (French Pat. 363,846, 1906) claim the employment of the acetyl-derivatives of polychlor-alkylanilines and also symmetrical methylbenzoyltrichloranilide as substitutes for camphor.

L. Arbezcarme (French Pat. 372,512, 1906) patented the use of rosin and naphthaline.

Chem. Fabrik vorm. Weiler-Tei Meer (Eng. Pat. 16,271, 1906) include carboxylic acid derivatives (formyl, acetyl, ethoxalyl, and benzoyl) of secondary aromatic amines as suitable for partial or entire replacement of the camphor.

F. Bayer & Co. (Eng. Pat. 14,634, 1910) state that pentachloroethylene has very little solvent action upon nitro-cellulose, but in conjunction with alcohol or other solvent it behaves in the same way as camphor, producing a plastic mass which can be moulded or worked. With acetyl cellulose and suitable solvents it forms plastic masses.

According to the patent of the E. J. Du Pont de Nemours Powder Co. (French Pat. 449,606, 1912) a colloidal product can be formed by mixing together a carbon compound such as nitro-cellulose with an alcohol aldehyde, preferably one which is non-volatile and is capable of polymerizing, as, for example, acetaldol. A solution of camphor in a volatile solvent may also be added if desired. It is stated that the composition thus formed has a lower fusion temperature than the mixture of nitro-cellulose and camphor. A further claim (French Pat. 449,607, 1912) is for the preparation of solutions from nitro-cellulose and acetaldol. In their American patent (U.S. Pat. 1,234,921, 1917) the proportions given are pyroxylin with 2 to 40 per cent. of aldol and 10 to 60 per cent. of vegetable oil, such as castor oil, the proportion of aldol and oil together amounting to 40 to 75 per cent. of the total constituents.

Another patent granted to the Du Pont Co. (U.S. Pat. 1,161,063, 1915) is for the use of a benzoic ester of phenol (phenyl-benzoate) or an ester of a homologue of phenol for producing with pyroxylin a colloidal material.

C. Gillet Aîné (French Pat. 382,350, 1906) claimed the use of a mixture of rosin and castor oil to replace a portion of the camphor.

Soc. Anon. Nouvelle "L'Oyonnithe" (French Pat. 387,179, 1908) state that the camphor can be partly or entirely replaced by the methylic, ethylic, and other esters of fatty acids, *e.g.* palmitic, stearic, oleic acids.

The patent granted to the Chem. Fab. Greishem, Electron. (Eng. Pat. 15,855, 1909) claims the use of dihydroxyphenylsulphone as a substitute for a part or the whole of the camphor.

F. Boehringer und Söhne (Ger. Pat. 214,962, 1906) replace either the whole or a portion of the camphor by cyclic ethers obtained by condensing aldehydes or lactones with polyhydric alcohols of the general formula $CH_2OH(CHOH)XCH_2OH$, as, for example, methylene

ethylene ether, ethylidene glycol ether, methylene-glycerol, acetonyl-glycerol, benzylidene glycol, erythri-diformal, diactone-arabitol, or triacetone-mannitol.

P. Breteau and H. Lerouse (French Pat. 409,557, 1909) claim the whole of the following substances as substitutes for camphor:—Aromatic aldehydes, as, for example, pure or commercial benzaldehyde, homologous alkylated or arylated derivatives, hydro-aromatic lactones, such as hexahydroxybenzylketone, tetrahydroxybenzylketone, and their alkylated derivatives, hydroxynaphthyl ketones, etc.

B. G. Buchstab (Ger. Pat. 214,398, 1908) blows air through a solution of gun-cotton, and replaces the evaporated solvent with methyl-alcohol or other suitable liquid. The material is then mixed with lactic acid or its salts, or with strontium chloride and a small quantity of castor oil, the product being worked like celluloid without the addition of camphor.

The Badische Anilin und Soda also claim the use of an acyl derivative of a completely hydrogenized aromatic base in the manufacture of a material resembling celluloid (Eng. Pat. 9270, 1914). They give as an example of such a composition:—70 parts of nitro-cellulose, 30 parts of *p*-toluene-sulphodicyclohexylamine, and sufficient alcohol to convert the material into a plastic mass like celluloid.

Solvents of Pyroxylin.—A very large number of solvents for nitro-cellulose have been suggested or used for the preparation of plastic masses or solutions, these being recorded in patent specifications and other literature on the subject. It would serve no useful purpose to enumerate the whole of these, but a very long list will be found in a paper by H. de Mosenthal.* Some of the more interesting ones are mentioned below, they are not all solvents *per se*, but in some cases they are used in combination:—

Acids.—Nitric acid at 80° C., sulphuric acid, glacial acetic acid, butyric acid.

Alkalies or Basic Substances and Derivatives.—Ammonia dissolved in ethyl ether. After moistening with alcohol, addition of caustic alkalies or sulphides of sodium, potassium and ammonium. Aniline, pyridine. Anilides such as formanilide, acetanilide, etc.

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* *Journ. Soc. Chem. Indt.*, 1904, p. 295.

Esters.—This is a very large class, including ordinary ether, methyl, ethyl, propyl, butyl, and amyl esters of formic, acetic, butyric, valerianic, lactic, oxalic, succinic, sebacic, tartaric, citric, benzoic and other acids. Nitric and hydrochloric esters, amyl nitrate, methyl nitrate. Nitro-glycerine, nitromannite, acetins, etc., etc.

Alcohols.—Methyl, ethyl, propyl, isobutyl, and amyl alcohols and mixtures of these with the above ethers, with acids, aldehydes, nitrophenols, amidophenols, pyridine, etc., etc.

Ketones.—Acetone, diethyl-ketone, propione, etc., etc. Acetone oils mixed with benzaldehyde.

Aldehydes.—Methylal, acetal, iso-valeric aldehyde, etc.

Hydrocarbons.—Benzene, petroleum spirit.

Terpenes and Derivatives.—Camphor, borneol, nitro-, chloro-, bromo-, chloronitro- and bromonitro derivatives of camphor. Thujone, pulegone (oil of peppermint), oil of camphor, ozonized oil of turpentine, artificial camphor, nitrated resin oils and resins, camphor dissolved in alcohol, hydrocarbons, ether, sulphurous acid, carbon bisulphide, carbon tetrachloride.

In the earlier patent specifications we find the following:—

John MacIntosh (Eng. Pat. No. 1090, May, 1858) used equal parts of wood spirit and coal naphtha.

Parkes (Eng. Pat. No. 2675, 1864) claimed the use of wood naphtha strengthened by distillation over fused calcium chloride. Parkes also mentions as solvents, nitrobenzene, aniline, glacial acetic acid, and camphor dissolved in methyl alcohol or alcohol-ether.

H. Parkes (Eng. Pat. 1866, May 10, 1886) mentions as solvents camphor with sulphurous acid, turpentine, benzoline, gasoline, or other light spirit, mineral oil or naphtha, carbon bisulphide, tetrachloride of carbon, ether, or wood spirit.

Spill (Eng. Pat. No. 3102, 1869) gives camphor in alcohol, camphor oil, aldehyde, and a mixture of aldehyde and alcohol as solvents for pyroxylin.

Hyatt uses fused camphor as a solvent. Pelouze* mentions ethyl and methyl acetates as solvents, while Dominte and Merard† employed ether-alcohol.

John H. Stevens, in a series of American patents quickly following each other (U.S. Pats. 269,340; 269,341; 269,342; 269,344, and 269,345 of 1882), claims a large number of solvents, including the following:—Methyl nitrate, ethyl butyrate, ethyl valerate, ethyl benzoate, ethyl formate, methyl salicylate, amyl formate, amyl acetate, amyl butyrate, amyl valerate, ethyl sebacylate, dinitrobenzene, coumarin, amyl nitrite in alcoholic solution.

Robert Schupphous also took out several patents (U.S. Pats. 410,205; 410,206; 410,207; 410,208; 410,209 of 1889) in which he claims the use of propyl and isobutyl alcohols with camphor, alpha and beta naphthol with alcohol, and anthraquinone with alcohol. Iso-valeric acid and its derivatives, amyliden-dimethyl and amyliden-diethyl ethers, all of which are said to be efficient solvents for nitro-cellulose.

August Sayer (U.S. Pat. 470,451, 1892) states that diethylketone, dibutylketone, dipentylketone, and the compound ketones, methylpropyl, methylbutyl, methylamyl, and ethylbutyl are powerful solvents.

Leonard Paget (U.S. Pats. Nos. 494,792; 494,793) claims the use of methylamyl oxide as a solvent for nitro-cellulose, but states that ethylamyl oxide is not a solvent. Among more recent patents the following are worth noting:—

R. N. Riddle (U.S. Pat. 797,373, 1905) claims phenyl acetate as a solvent for nitro-derivatives of the carbohydrates including nitro-cellulose.

W. G. Lindsay, Assignor to the Celluloid Co., New York (U.S. Pats. 1,027,617 and 1,027,618, 1912), claims the use of ethylene-chlorhydrin and ethylene-acetochlorhydrin, with or without other diluents, colouring matters, or inert substances.

J. M. Sauverzac (French Pat. 402,950, 1908) dissolves the nitro-cellulose in a solution of a metallic chloride in alcohol. As example: a solution of 10 grams of aluminium chloride in 100 c.c. of alcohol is employed for dissolving 50 grams of nitro-cellulose. It is stated that this solution can be diluted with 80 per cent. of water without precipitating, and that the solution is very suitable for spinning threads, yielding a fibre which is quite supple and elastic.

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* *Compt. rend.*, 24, 2.

† *Ibid.*, 29, 390.

J. Duclaux (French Pat. 439,721, 1912) states that methyl and ethyl formates are excellent solvents for nitro-cellulose, and that dilution with an equal weight of methyl or ethyl alcohol does not materially affect their action. These solutions can be spun into a fibre, and methods and apparatus for recovering the solvent are described.

F. Kniffen, Assignor to E. D. du Pont de Némours Powder Co. (U.S. Pat. 1,118,494, 1914), claims the use of a solvent consisting substantially of equal parts of ethyl acetate and benzene.

The Badische Anilin und Soda Fabrik (Ger. Pat. 251,351, 1911) claim the use of the esters of completely hydrogenized phenols, with or without addition of other substances as solvents for cellulose esters or celluloid. As examples they mention cyclohexanol formate or acetate, and methyl-cyclohexanol formate which can be prepared cheaply and are efficient solvents. They state that varnishes prepared with these solvents evaporate or dry sufficiently quickly, leaving resistant, elastic coatings, which do not appreciably affect the appearance of the material upon which they are applied.

The British and Continental Camphor Co., Ltd. (French Pat. 428,664, 1910), employ ethyl and methyl butyrate instead of amyl acetate as solvents for preparing varnishes, etc.

Walter D. Field, in his paper, elsewhere referred to, states that the solvents may be grouped in several ways, which shortly are as follows:—

1. *General Classification.*—(*a*) Those which act in the cold and without solution in alcohol. (*b*) Those which require solution in alcohol.

2. *Chemical Classification.*—(*a*) Monhydric alcohols.

(*b*) Compound ethers of the fatty acids with monhydric alcohols. (*c*) Aldehydes. (*d*) Simple and mixed ketones of the fatty acid series. Most of the solvents for pyroxylin fall into one or other of these four classes, except the following:—Amyl nitrate and nitrite, methylene-dimethyl ether, ethylene-diethyl ether, amyl chloracetate, nitrobenzene and dinitrobenzene, coumarin, camphor, glacial acetic acid, and mono-, di- and tri-acetin.

A third classification distinguishes the solvents as hygroscopic or non-hygroscopic, a most important distinction, as will soon be realized. To the first class belong acetone, methyl acetate, ethyl acetate, methyl alcohol, aldehyde, ethyl formate, propyl formate and propyl acetate. Nitrocellulose in these solvents absorbs moisture from the atmosphere and thus yields films which are cloudy on the surface, in some cases this cloudiness penetrates throughout the film. In this connection he quotes the following from Dr. Guido Wolfram:* "Pentanitro-cellulose is soluble in acetone acetic ether, and still easier in a mixture of the same with ethyl-ether. The solution gives a cloudy layer—a proof that the obtaining of a vitreous layer depends not only on the substance, but likewise on the kind of solvent used." To this Field adds the following remark: "If Wolfram had used alcohol instead of ether in combination with the hygroscopic solvents, he would have obtained clear transparent or glassy films on the evaporation of the solvent by reason of the alcohol absorbing the water and preventing the precipitation of the pyroxylin. All the non-hygroscopic active solvents of pyroxylin deposit it from solution as a transparent film." The solvents most commonly employed for nitro-cellulose are acetone, amyl acetate, and camphor in alcohol with or without other additions or diluents, the properties of which are given in the following pages.

SOLVENTS.

Alcohol. Ethyl Alcohol. C_2H_5OH.—Ordinary alcohol is prepared by the fermentation of a solution of sugar, molasses, glucose, or saccharified starch from grain, potatoes, etc., by means of yeast. It is purified by distillation and rectification, and then appears as a clear, mobile liquid, having a pleasant odour and a sharp, hot taste. It is readily inflammable, burning with a blue, almost invisible flame.

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* *Ding. Poly. Journ.*, 230, 156.

The specific gravity of pure alcohol is 0·7935 at 15° C., and it boils at 78°·4 C.

The term "absolute alcohol" is often applied to alcohol of 95 per cent. strength and upwards.

The following are the strengths of commercial alcohol:—

Rectified Spirit of the British Pharmacopœa	Specific gravity	0·8382–84 per cent. of alcohol.	
Spirit 61° over proof.	,,	0·8272 at 15·5° C.	88 per cent.
,, 64° ,,		0·8215 ,,	90 ,,
,, 67° ,,		0·8152 ,,	93 ,,
Absolute alcohol		0·808 ,,	95 or over.
Pure alcohol		0·79384 ,,	100 per cent.

Castor oil, which is used in the manufacture of celluloid varnishes, is freely soluble in alcohol, differing in this respect from almost all other oils.

Methylated Spirit.—In order to allow the use of alcohol for manufacturing and domestic purposes duty free it is methylated, that is to say, certain substances are added to it with the object of rendering it unfit for drinking purposes without impairing its usefulness for most other applications.

In this country two kinds of methylated spirit are allowed by the excise authorities to be made and used:—

1. For manufacturing purposes only and under special licence, consisting of 19 parts of pure alcohol and 1 part of wood spirit.

2. For household and general use, consisting of 90 parts of alcohol, 10 parts of wood spirit, and $\frac{3}{8}$ per cent. of mineral naphtha. This may be obtained retail in almost any quantities.

Methylated spirit is usually sold in two strengths:—

64° over proof, specific gravity 0·8215, 94 per cent. of alcohol.
61° ,, ,, ,, 0·8272 92 ,, ,, ,,

It can, however, be obtained in higher strengths up to 67° over proof, specific gravity 0·8154, containing 95 to 96 per cent. of alcohol.

Ether. Ethyl Ether. $(C_2H_5)_2O$.—Sometimes known, though erroneously, as sulphuric ether. Is prepared by heating ethyl-alcohol with sulphuric acid.

Ether is an extremely mobile, colourless and volatile liquid with a pleasant, characteristic odour. Specific gravity 0·720, boiling point 34·9° C., leaving when pure no residue on evaporation. Usually contains a little water, alcohol, and other impurities, including ethyl peroxide, which explodes with violence spontaneously even at 100° C.; for this reason it should be carefully rectified. Very inflammable, and the vapour when mixed with air is extremely explosive. Usually contains 92 to 94 per cent. of real ether.

Wood Spirit. Wood Naphtha.—Obtained in the dry distillation of wood. Consists principally of methyl alcohol CH_4O (50–90 per cent.) with more or less acetone, allyl alcohol, furfural, various ketones, etc. Has a characteristic rather unpleasant odour.

Methyl Alcohol. $CH_3.OH$.—Produced by the careful rectification of wood spirit. Is a clear, colourless liquid having a pleasant odour similar to that of ordinary alcohol. Very volatile, and evaporates at the ordinary temperature in an open dish leaving no residue. Boiling point 65° C., specific gravity at 15·5° C. 0·796.

Amyl Alcohol. $C_5H_{11}.OH$.—Is one of a large series of aliphatic alcohols, and is prepared by the fractional distillation of "fusel oil," the residue left after the rectification of ordinary alcohol being more abundant in the spirit obtained from potatoes than that from grain.

There are several isomeric amyl alcohols which differ from one another in their physical and chemical properties. The normal amyl alcohol, boiling at 137° C., and having a specific gravity of 0·820, while iso-amyl alcohol boils at 131° C., and has a specific gravity of 0·8148. The latter is the principal constituent of fusel oil, and therefore the one known ordinarily as amyl alcohol. It is a colourless, rather viscous liquid, having a peculiar, rather suffocating odour.

Amyl Acetate. $C_5H_{11}.C_2H_3O_2$.—Is an ether obtained by heating together in a retort, amyl alcohol, sodium acetate, and concentrated sulphuric acid. The ether distils over, and is purified by redistillation. It is a colourless, limpid liquid with a fragrant odour closely resembling that of jargonelle pears. Its specific gravity is 0·8774 at 15° C., boiling point 148° C. In contact with air it volatilizes slowly but completely. It burns when heat is applied, but not readily.

Acetone. $CH_3.CO.CH_3$.—Is contained in wood spirit, from which it can be obtained by careful rectification. It is, however, usually prepared by the dry distillation of an acetate, such as acetate of lime, but cannot be obtained from acetate of soda. Mobile, colourless liquid having a peculiar ethereal odour. Specific gravity 0·797 at 15° C.; boiling point 56° C. Burns readily when a flame is applied.

Guttman found commercial acetone to have a specific gravity of 0·7965, and a boiling point of 56·2° to 56·4°. When free from aldehyde it gives no reaction with a dilute solution of potassium permanganate, and the acidity is usually not higher than 0·00225 per cent., calculated as acetic.

Nitrobenzene. Nitrobenzol. Oil of Mirbane. $C_6H_5.NO_2$.—Is obtained by adding benzene slowly to fuming nitric acid or a mixture of sulphuric and nitric acids, keeping the mixture cool to prevent decomposition. The product is washed with water and then distilled. It is a heavy, yellowish liquid having an odour resembling that of benzoic aldehyde or oil of bitter almonds. Specific gravity 1·2, and boiling point 210° C.

Ether Alcohol.—This is simply a mixture of ether and alcohol in various proportions.

DILUENTS.

In the preparation of varnishes from pyroxylin, after dissolving the nitro-cellulose in one of the above solvents or a mixture, it is often diluted with a liquid which is not a solvent, with a view either to cheapen the product or to increase its drying properties. The liquids usually employed for this purpose are benzol and petroleum spirit.

Benzol. Coal-tar Naphtha.—The lightest and most volatile hydrocarbon obtained from coal tar by distillation is known as benzol or coal-tar naphtha. This distils mostly below 100° C. At 110°–120° C. toluene or toluol passes over, and at a still higher temperature xylenes and other homologues. The boiling point varies between 80° and 120° C., and its specific gravity is about 0·885. It has a pronounced "gassy" odour, and is easily inflammable at the ordinary temperature, burning very vigorously with a reddish, smoky flame.

By rectification it yields:—

Benzene C_6H_6.	Boiling point	79°;	Specific gravity 0·884 at 15° C.
Toluene C_7H_8	,,	110°	
Xylenes C_8H_{10}	,,	137°–140°	
Cumene, etc.	,,	153°	

Good commercial benzol distils almost entirely between 80° and 82° C.

There are in commerce several grades of benzol known as 90ˢ benzol, 50/90ˢ benzol, and 30ˢ benzol, these figures denoting the percentages which distil over below 100° C.

Benzine, Petroleum Spirit.—Is the light spirit obtained in the distillation of American petroleum. The very lightest spirit of all is known in America as gasoline, and that which distils after petrol is the ordinary paraffin oil used for burning, known as kerosene. Petroleum spirit has not a definite composition, but consists of a mixture of several hydrocarbons, principally hexane (C_6H_{14}), heptane (C_7H_{16}), and octane (C_8H_{18}), has a specific gravity of 0·730 to 0·760, and boils between 40° and 75° C. It is a clear, colourless liquid possessing a peculiar petroleum odour, and burns vigorously with a smoky flame.

A sample examined by G. H. Hurst gave the following figures by fractional distillation:—

	Per cent.
Below 70° C.	3
75°	12
80°	24
85°	30
90°	49
95°	55
100°	66
105°	72
110°	81
120°	92

Petroleum spirit volatilizes completely on exposure to air, but leaves a slight odour which persists for a very long time.

SPECIFIC GRAVITY OF SULPHURIC ACID AT 60° F.

Specific Gravity.	Degrees Twaddle.	Percent. of H_2SO_4.	Pounds of H_2SO_4 per gallon.	Specific Gravity.	Degrees Twaddle.	Percent. of H_2SO_4.	Pounds of H_2SO_4 per gallon.
1·200	40	27·32	3·24	1·735	147	80·24	13·90
1·225	45	30·48	3·73	1·740	148	80·68	14·00
1·250	50	33·43	4·20	1·745	149	81·12	14·10
1·275	55	36·29	4·60	1·750	150	81·56	14·27
1·300	60	39·19	5·00	1·755	151	82·00	14·40
1·325	65	42·08	5·50	1·760	152	82·44	14·50
1·350	70	44·82	6·00	1·765	153	82·88	14·60
1·375	75	47·47	6·40	1·770	154	83·32	14·75
1·400	80	50·11	7·00	1·775	155	83·90	14·90
1·425	85	52·63	7·50	1·780	156	84·50	15·00
1·450	90	55·03	8·00	1·785	157	85·10	15·20
1·475	95	57·37	8·40	1·790	158	85·70	15·30
1·500	100	59·70	9·00	1·795	159	86·30	15·50
1·525	105	62·00	9·45	1·800	160	86·90	15·64
1·550	110	64·26	10·00	1·805	161	87·60	15·81
1·575	115	66·30	10·44	1·810	162	88·30	15·98
1·600	120	68·51	11·00	1·815	163	89·05	16·21
1·625	125	70·74	11·85	1·820	164	90·05	16·40
1·650	130	72·87	12·00	1·825	165	91·00	16·60
1·675	135	74·97	12·50	1·830	166	92·10	16·90
1·700	140	77·17	13·10	1·835	167	93·43	17·20
1·705	141	77·60	13·22	1·840	168	95·60	17·60
1·710	142	78·04	13·23	1·8410	168	97·00	17·80
1·715	143	78·48	13·25	1·8415	168	97·70	18·00
1·720	144	78·92	13·67	1·8410	168	98·20	18·00
1·725	145	79·36	13·69	1·8400	168	99·20	18·25
1·730	146	79·80	13·81	1·8390	168	99·70	18·34
				1·8385	168	99·90	18·40

SPECIFIC GRAVITY OF NITRIC ACID AT 60° F.

Specific Gravity.	Degrees Twaddle.	Percent. of HNO_3 by weight.	Pounds of HNO_3 per gallon.	Specific Gravity.	Degrees Twaddle.	Percent. of HNO_3 by weight.	Pounds of HNO_3 per gallon.
1·100	20	16·80	1·848	1·320	64	50·63	6·683
1·105	21	17·57	1·941	1·325	65	51·40	6·810
1·110	22	18·35	2·037	1·330	66	52·24	6·948
1·115	23	19·12	2·132	1·335	67	53·09	7·087
1·120	24	19·89	2·227	1·340	68	53·94	7 228
1·125	25	20·67	2·235	1·345	69	54·79	7·369
1·130	26	21·44	2·423	1·350	70	55·64	7·511
1·135	27	22·21	2·520	1·355	71	56·53	7·660
1·140	28	22·98	2·620	1·360	72	57·42	7·809
1·145	29	23·76	2·720	1·365	73	58·31	7·959
1·150	30	24·53	2·821	1·370	74	59·21	8·112
1·155	31	25·30	2·922	1·375	75	60·10	8·264
1·160	32	26·08	3·025	1·380	76	61·00	8·418
1·165	33	26·85	3·128	1·385	77	61·97	8·583
1·170	34	27·62	3·231	1·390	78	62·95	8·750
1·175	35	28·40	3·337	1·395	79	63·92	8·917
1·180	36	29·17	3·442	1·400	80	64·90	9·086
1·185	37	29·94	3·548	1·405	81	66·01	9·274
1·190	38	30·71	3·654	1·410	82	67·12	9·464
1·195	39	31·49	3·763	1·415	83	68·23	9·653
1·200	40	32·26	3·871	1·420	84	69·34	9·846
1·205	41	33·02	3·919	1·425	85	70·45	10·04
1·210	42	33·79	4·088	1·430	86	71·83	10·27
1·215	43	34·55	4·198	1·435	87	73·21	10·50
1·220	44	35·32	4·309	1·440	88	74·59	10·76
1·225	45	36·08	4·442	1·445	89	75·98	10·97
1·230	46	36·85	4·532	1·450	90	77·36	11·22
1·235	47	37·61	4·645	1·455	91	78·75	11·46
1·240	48	38·38	4·759	1·460	92	80·13	11·70
1·245	49	39·15	4 874	1·465	93	81·52	11·95
1·250	50	39·91	4·988	1·470	94	82·90	12·19
1·255	51	40·68	5·105	1·475	95	84·28	12·43
1·260	52	41·44	5·221	1·480	96	85·66	12·68
1·265	53	42·21	5·328	1·485	97	87·05	12·93
1·270	54	42·97	5·457	1·490	98	88·43	13·18
1·275	55	43·74	5·577	1·495	99	89·82	13·43
1·280	56	44·50	5·696	1·500	100	91·20	13·68
1·285	57	45·27	5·817	1·505	101	92·66	13·94
1·290	58	46·04	5·939	1·510	102	94·13	14·21
1·295	59	46·80	6·060	1·515	103	95·59	14·48
1·300	60	47·57	6·184	1·520	104	97·06	14·75
1·305	61	48·33	6·307	1·525	105	98·53	15·02
1·310	62	49·10	6·432	1·530	106	100·00	15·30
1·315	63	49·86	6·556				

CHAPTER III

THE MANUFACTURE OF CELLULOID

HISTORICAL

THE action of nitric acid upon starch, woody fibre, and other carbohydrates was first investigated by Braconnot in 1832, who found that they were converted by it into easily inflammable substances, to which he applied the name "Xyloïdine." In 1832 Pélouze confirmed the results of Braconnot and further discovered that paper, linen, and cotton, after treatment with concentrated nitric acid in the cold, and then washing with water, although unaltered in appearance, had become highly explosive.

Schönbein was the first to apply this knowledge to practical use by manufacturing "cotton powder" or "gun-cotton," as he termed it, which could be used in place of gunpowder. This was prepared by soaking carded cotton wool in the strongest nitric acid, then washing in a stream of water until entirely free from acid, and drying at a low temperature.

The "gun-cotton" thus prepared was found to have distinct advantages since, containing as it does no mineral matter it left no residue on explosion, and was therefore practically smokeless. Similar products were subsequently independently prepared by Böttger and Otto.

The use of sulphuric acid in admixture with nitric acid, due to Knop, is now universal.

In 1847 Maynard discovered that nitro-cellulose, although insoluble in alcohol and in ether, dissolved quite readily when the two were mixed. This solution was named by him "collodion," which name it still retains.

Collodion was soon found to be extremely useful in surgery as an airtight cover for wounds and sores, also for coating bottle stoppers and the preparation of thin capsules.

In 1850 collodion was introduced into photography by Scott Archer in his "wet collodion" process, an entirely new process which completely revolutionized the methods in this industry, and laid the foundations of modern photography. It is still used as a coating for some kinds of sensitized papers, and has certain advantages over gelatine which later replaced it when dry plates came into use. Celluloid is now used on an extensive scale for photographic films, and is indispensable for roll film cameras and for kinematograph work.

In 1854 James A. Cutting of Boston patented the employment of camphor in photographic emulsions, made with collodion (Eng. Pat. 1638, July 26, 1854) the object being to increase the intensity and clearness of the photographic image, which, as we now know that camphorated spirit is a better solvent of pyroxylin than ordinary spirit, no doubt it did by rendering the film more transparent. This is the first mention of camphor in association with pyroxylin.

In 1860 a patent was granted to Stephen Barnwell and Alexander Rollason (Eng. Pat. 2249, September 15, 1860) for "Improvements in the preparation of hard, resistant, adhesive, plastic, or resilient compounds, and articles unalterable in their nature and varied in colour, which said compounds in a state of solution may also be advantageously employed as paints and varnishes." The patentees combine "pyroxylene," made as described, with oils, essential, animal, vegetable, and mineral; gums, tar, bitumen, cements, wax and grease; ivory and bone dust; powdered bark; farinaceous and amylaceous substances; and vegetable or mineral pigments, and bronzes, and, in addition, india-rubber and gutta-percha dissolved in chloroform and carbon bisulphide, ether and alcohol, and "all anhydrous basic salts that may be soluble or that will in any way combine with the pyroxylene, iodide of potassium and cadmium, and oxides of metals capable of imparting colour."

Alexander Parkes of Birmingham took out a patent in 1855 (Eng. Pat. 2359, October 22, 1855) for a composition for moulding purposes. This patent is devoted principally to rubber compositions, but in it he claims the use of a gun-cotton solution, either alone or in admixture with india-rubber or gutta-percha, for casting in moulds, or for converting into sheets, the inflammability of the product being reduced by the addition of phosphate of ammonia or magnesia, cadmium iodide, calcium oxalate, talc, or mercuric iodide.

Parkes subsequently took out several patents relating to nitro-cellulose compositions or "Parkesine" as he termed it. The patent of 1864 (Eng. Pat. 2675, October 24, 1864) is for a plastic composition produced by dissolving nitro-cellulose in wood naphtha, which is used alone or in admixture with castor oil, cotton-seed oil, or linseed oil, gum balata and other gums and resins, such as shellac, copal, and animi. To render the material non-inflammable, zinc chloride, sodium tungstate or gelatin dissolved in acetic acid, is added. In the patent of 1865 (Eng. Pat. 1313, May 11, 1865) for the production of collodion and compounds known as "Parkesine" the ordinary solvents are replaced by glacial acetic acid, aniline, or nitro-benzene, or camphor is added to the solvents ordinarily employed.

As an example: 100 parts of pyroxylin are moistened with a solvent such as wood naphtha distilled over calcium chloride, any excess being removed by pressure, and 10 to 50 parts of nitro-benzene, 10 to 50 of camphor, and 150 to 200 of vegetable oil are added, the whole being mixed by means of steam-heated rolls, gums, resins, bituminous substances, india-rubber and gutta-percha being in some cases added. When acetic acid is used as a solvent, gelatine, gums, and resins can also be incorporated. In this case the proportions recommended are 100 parts of pyroxylin and 50 parts of acetic acid for a stiff paste, or 100 to 300 parts of acetic acid for a thin paste. For an insulating material for telegraph wire he uses 100 parts of pyroxylin and 100 parts of india-rubber or gutta-percha dissolved in nitrobenzol or aniline. For photographic purposes the collodion solution in nitro-benzol or aniline is used together with an ethereal solution of the same material.

A later patent in 1865 (Eng. Pat. 3163, December 8, 1865) relates to the use of a centrifugal machine for removing the acids after nitrating, and to machinery for mixing the xyloïdine—after dissolving in naphtha or other solvents—with the other ingredients, also steam-heated rollers for working the product, the machinery being figured and described.

The patent of 1866 (Eng. Pat. 2709, October 19, 1866) relates to a method of treating the xylonite in a vessel provided with rotating agitators, the nitro-cellulose in solution being precipitated in this vessel by the addition of water or naphtha in the form of curdlike masses which are pressed and rendered plastic by passing through heated rollers. Imitation pearl is made by incorporating pearly material, but preferably fish scales, with the composition, and artificial ivory by placing together two sheets, the one clear white, the other coloured with strontium carbonate, or similar substance, and passing them through internally heated rollers, which amalgamates the two.

A later patent taken out by Parkes (Eng. Pat. 1614, May 16, 1868) embodies the use of white starch, wheat flour, or cotton fibre in combination with pyroxylin, dissolved as previously described, for the manufacture of billiard balls, the solvent being removed by soaking in such liquids as carbon bisulphide, chloride of carbon, or benzene, which are subsequently eliminated by treatment in a vessel from which the air is exhausted.

Daniel Spill invented a product which was probably celluloid, and he manufactured and sold it under the name of Xylonite on a large scale for some years as a substitute for ivory, horn, tortoise-shell, etc.

Spill's first patent (Eng. Pat. 2666, September 21, 1867) claims the use of alcoholic solutions of substances insoluble, or nearly so, in water, such as fixed oils, vegetable oils, essential oils, resins, gum resins, spirits of turpentine, fats, light oils, and coal and mineral naphthas as solvents of xyloïdine. In the patent of 1868 (Eng. Pat. 3984, 1868) he claims the preparation of xyloïdine by employing non-volatile solvents such as animal, fish, vegetable, or mineral oils, mineral tar, lard oil, cod-liver oil, camphor oil, or liquid camphor, linseed, or heavy coal oils, or mixtures of these, and mentions also that any of the following may be added: paraffin, camphor, resins, fat, wax, india-rubber, gutta-percha or belata gum, either alone or in admixture. As an example of his invention he cites the following formula:—

	Parts by Weight.
Camphor, camphor oil, or liquid camphor . . .	20
Oil, such for example, as castor or linseed oil, either before or after such oils have been oxidized or boiled	40
Xyloïdine	40

Similar claims are made in Spill's American patents (U.S. Pats. 91,337 and 91,378, 1869).

Another patent was taken out by Spill in 1869 (Eng. Pat. 3102, October 26, 1869) in which he claims the use of a number of solvents of xyloïdine, including "camphor or camphor oil, or mixtures of the two with hydrocarbons obtained in the distillation of petroleum, or the products of the distillation of coal, shale, or other bituminous substances, which products have boiling points from about 200° to 400° F.; or castor oil, with or without alcohol or spirits of wine; carbon bisulphide with alcohol; aldehyde alone or with alcohol or methylated spirit." Xyloïdine is dissolved in any of these solvents and the solution is incorporated with animal, fish, vegetable, or mineral oils, oxidized or otherwise, or with mixtures of these oils with paraffin, camphor, resins, fat, wax, etc., to produce a material which may be used alone or with pigments, etc., for various purposes, such as the covering or protecting of telegraph wires. Or the xyloïdine may be merely softened by the solvents and then incorporated with the other substances.

As an example of his invention he gives the following:

	Parts by Weight.
Xyloïdine	27
Castor oil	27
Camphor	6

and any of the above solvents 40 parts by weight.

Similar claims are made in the American patent (U.S. Pat. 97,454, November 30, 1869).

In 1875 Spill took out a further patent (Eng. Pat. 1739, May 11, 1875) for the use of nitro-cellulose compounds, in which the soluble gun-cotton or xyloïdine is dissolved in one of the solvents mentioned in previous specifications, the compound being spread on the surface by a machine, or made into tubes. The manufacture of imitation tortoise-shell, etc., by printing on designs, or the incorporation of differently coloured sheets by pressure is also included.

Other patents taken out by Spill were for bleaching xylonite (Eng. Pat. 180, 1870) also for evaporating the solutions of xyloïdine to remove the solvent and thus produce stiffer products and at the same time recover the solvents (Eng. Pat. 787, 1870 and U.S. Pat. 101,175, 1870) and lastly Pat. Nos. 1626, June 14, 1870; 1017, April 6, 1870 and 2649, October 6, 1870 (the last two in conjunction with W. J. Henley), but these do not disclose anything materially novel.

John Wesley Hyatt, of New York, was also experimenting with nitro-cellulose compositions, and, according to a statement which was made by Prof. Chandler at the presentation of the Perkin Medal to Hyatt,* he proceeded upon quite independent lines knowing nothing of the work of Parkes and Spill. Hyatt commenced the manufacture of billiard balls by moulding a core of plastic material and covering it with a layer of nitro-cellulose dissolved in a mixture of ether and alcohol. In 1870 the business was established and proved very successful. In 1869 Hyatt took out a patent (U.S. Pat. 88,633, April 6, 1869) for a moulding composition to imitate ivory and similar products, composed of fibrous materials and gum shellac or other solid fusible adhesive gum. Other patents quickly followed. The patent (U.S. Pat. 88,634, April 6, 1869) claims an improved method of coating billiard balls, consisting in dipping balls made of some suitable composition in a solution of collodion, to which any desired colour can be imparted by the previous addition of appropriate colouring matters. The patent (U.S. Pat. 89,582, May 4, 1869) was for a composition consisting of ivory dust or similar substance with collodion and subjecting to pressure during the evaporation of the solvent. The patent (U.S. Pat. 91,341, June 15, 1869) taken out by Hyatt and his brother, related to the manufacture of a plastic collodion by using very little solvent, and submitting the product to heavy pressure while moulding, thus saving valuable solvent and economizing time. In their patent of 1870 (U.S. Pat. 105,338, July 12, 1870) "Improvement in treating and moulding pyroxyline," the brothers Hyatt claim the method of manufacturing a solid product from nitro-cellulose and camphor, their three claims being: 1. Grinding pyroxylin into a pulp, as and for the purpose described. 2. The use of finely comminuted camphor gum mixed with pyroxylin pulp, and rendered a solvent thereof by the application of heat, substantially as described. 3. In conjunction with such use of camphor-gum the employment of pressure, and continuing the same until the mould and contents are cooled, substantially as described.

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* *Journ. Soc. Chem. Indt.*, 1914, p. 225. See also reply by Robert C. Schüpphaus, Ph.D., *ibid.* 1914, p. 678.

Thus, in the manufacture of their product which they termed "celluloid," the Hyatts used no solvent but only heat and pressure for combining the pyroxylin and camphor. Indeed in this patent they disclaim the use of alcohol as the following quotation shows: "The product is a solid, about the consistency of sole leather, which subsequently becomes as hard as horn or bone by the evaporation of the camphor. Before the camphor is evaporated the material is easily softened by heat and may be moulded into any desired form, which neither changes nor appreciably shrinks in hardening. We are aware that camphor made into a solution with alcohol, or other solvent of camphor, has been used in a liquid state as a solvent of xyloïdine. Such use of camphor as a solvent we disclaim."

The specification fixes the proportion at about one part of camphor to two parts of pyroxylin. Modifications of this process were subsequently patented (U.S. Pats. 156,352 and 156,353). For further information the reader may be referred also to English patents of the Hyatt brothers, No. 2101, July 26, 1870; No. 1025, April 18, 1871 and No. 3101, October 21, 1872, and also to the two sources mentioned in the footnote to p. 74.

THE MANUFACTURE OF CELLULOID.

The fundamental principle underlying the manufacture of celluloid is the property of nitro-celluloses (gun-cotton or collodion cotton) of dissolving, under certain conditions, in camphor and forming therewith the new product in question. This solution takes place when nitro-cellulose is warmed, under pressure, with camphor or an alcoholic solution of the same, or when it is brought into contact at the ordinary temperature, with a solution of camphor in ether or wood spirit.

It is easy to understand that the manufacture of celluloid is not without danger, though, with ordinary care, the risks are not nearly so great as the opponents of celluloid originally tried to make out.

Among the least dangerous of the methods to be now described should be ranked that in which fused camphor is employed under pressure, since in this case the gun-cotton is kept in a wet state, and therefore almost free from risk, up to the moment when it is changed into celluloid by the camphor, whereby it loses the power of exploding.

It is open to question, however, whether celluloid is still prepared by this roundabout and lengthy method in Newark, the answer being probably in the negative, in view of the far more convenient methods of manufacture by the cold process.

The so-called alcohol process was formerly used in the Stains works, but suffered from the defect that the air-dried and rolled celluloid plates obstinately retained a considerable amount of alcohol, the centres being still moist even when the plates were quite dry externally.

The most dangerous is the Magnus method, both on account of the risk attending the drying of the cotton, and on the other hand of the volatility of the ether and the risk of an explosion of the ether-laden air in the absence of efficient ventilation and presence of a light.

With the exercise of sufficient care, these dangers can be reduced to a minimum. The method introduced at Stains, using wood spirit, is safe in so far that this spirit begins to boil only at 65° C., and is therefore less likely than ether, which boils at 35° C., to liberate explosive vapours at the ordinary temperature.

The reactions which take place in the formation of celluloid have not yet been fully explained. It is, however, improbable that the camphor and gun-cotton enter into chemical combination, since in observing the behaviour of burning celluloid, by igniting it and blowing out the flame, it is found to glow for a short time, strong fumes of camphor being at the same time given off. Apparently, in this case, the propagation of combustion is confined to the gun-cotton or collodion, the camphor being heated sufficiently to cause it to volatilize but not to ignite. This behaviour during incomplete combustion indicates that the camphor and gun-cotton exist in a separate state in celluloid. Hence the formation of celluloid must be classed along with the physical processes and as analogous to those concerned in the manufacture of leather for instance. The hides of animals when placed in contact with tannin are converted into leather, the tannin being precipitated or absorbed by the fibres of the skin, which it envelops and prevents them from sticking together during drying. This simple physical process, however, is accompanied by considerable changes in the properties of the animal fibres, the hard, stiff hide, liable to putrefaction, being converted into non-putrefactive, flexible, supple leather. Similarly, it may be imagined that, in the formation of celluloid, the pyroxylin dissolving in the camphor fills up the minute pores of the latter, and that this physical intimate combination and fusion of the two substances will probably also result in the fusion of their chemical properties.

MANUFACTURING CELLULOID BY THE AID OF HEAT AND PRESSURE.

1. *Hyatt's Process.*—The process of the brothers Hyatt, of New York, consists in dissolving gun-cotton in molten camphor. The nitro-cellulose for this purpose is prepared by treating satin paper with a mixture of nitric acid (2 parts) and sulphuric acid (5 parts), sprayed on to the paper as it is unwound from a roll. In this stage of the process the greater part of the paper is converted into nitro-cellulose or pyroxlin. It is next immersed in a trough filled with acid, in which it is left for some time, being then removed into a vessel where it is washed with water to remove the superfluous acid. The washed pyroxylin forms a plastic mass, which is collected into lumps, subjected to considerable pressure, dried and broken up again, the lumps being drained in a hydro-extractor, comminuted and mixed with the camphor.

According to other reports the washed and dried nitro-cellulose is put through a breaking machine along with water, the latter allowed to drain off, and the mass subjected to very powerful pressure in a perforated vessel to expel the rest of the water and furnish a comparatively solid body, which, however, must retain sufficient moisture to prevent ignition in the subsequent stages of treatment. This mass is mixed with the camphor under water, kneaded, rolled, mixed at the same time with colouring matters and with other substances that are not disclosed by the makers, the object being to impart certain properties, such as transparence, etc., to the product. The usual proportions of the mixture are: 1 part of camphor to 2 of pyroxylin, though other proportions also furnish good results. When mixing is complete the mass is well pressed, to expel any watery constituents still present, and in addition, to bring the particles of camphor and pyroxylin into still more intimate contact to facilitate the solvent action of the former. The dried and pressed mass is transferred to a mould of the desired form, in the upper aperture of which fits a plunger which is forced down on the mass in a hydraulic press. While the mass is still under pressure it is heated by steam to about 130° C., a lower temperature, however, being sufficient for small quantities.

Under this conjoint influence of heat and pressure the solvent action of the camphor is exerted in a high degree, and the formation of celluloid proceeds very rapidly, being completed almost as soon as the maximum temperature has been attained.

On leaving the press the celluloid is hard, but remains elastic, and can be resoftened by warmth or by dipping it in boiling water; it can be also cut into sheets of varying thickness.

2. *Tribouillet and Besancèle's Process.*—One hundred parts of pyroxylin are intimately mixed with 42–50 parts of camphor, the mixture being wrapped in a very strong cloth, then in a horsehair press-cloth and placed in a warm press. Steam is admitted into the jacket of the press, which latter is also provided with a chamber containing a water spray to condense the vapours of the solvent disengaged in the operation, and enable them to be recovered for use again. After an hour or more the cakes remaining in the press-cloths are transferred to a heated cylinder press, and thence to a chamber (measuring about 150 cub. ft.) containing calcium chloride or sulphuric acid to absorb moisture, and connected with an air-pump to facilitate the drying process.

MANUFACTURE OF CELLULOID BY DISSOLVING GUN-COTTON IN AN ALCOHOLIC SOLUTION OF CAMPHOR.

A weak alcoholic solution (about 1 part in 8) of camphor is used, this being capable of dissolving pyroxylin when hot, though not at the ordinary temperature.

The gun-cotton is ground to pulp, mixed with the necessary colouring matter, and pressed to expel the watery liquid. The solvent is next added, in the proportion of 1 part to 2 parts of the pyroxylin, and stirred up well, the whole being left in a covered vessel until the solvent has permeated the entire mass. This is a matter of no difficulty, the camphor solution dissolving its way in. Finally the mass attains the same consistency, etc., as that prepared under pressure as already described.

PREPARING CELLULOID BY THE COLD PROCESS.

Preparation with an Ethereal Solution of Camphor.—Fifty parts, by weight, of collodion cotton are placed in an earthenware vessel and suffused with a mixture of 100 parts of ether of sp. gr. 0·728 (or 100 parts, by volume, of ether and 5 of alcohol) and 28 of camphor. The vessel is covered with a loaded caoutchouc plate to prevent rapid volatilization of the ether, which cover is removed at intervals in order that the mixture may be stirred. The greatest care must be exercised in carrying out this process on account of the low boiling point (35° C.) and ready inflammability of the ether, constant and effectual ventilation being essential. In the Magnus works all the windows are kept open in the rooms where the celluloid is being made, in order to prevent any accumulation of ether vapour (which forms an explosive mixture with air). The mixture finally becomes a transparent, sticky, gelatinous mass. The bulk of the ether volatilizes during the process, and is not recovered.

Closed machines are now employed for mixing the pyroxylin with the solvent and other ingredients, to form a stiff paste. An horizontal form of machine by David

Bridge & Co., Ltd., is shown in Fig. 25. Fig. 26 is another type made by the same firm which can be used for the same purpose and also for preparing thinner solutions suitable for varnishes.

The crude celluloid is rolled between a pair of superimposed calendering rollers until it becomes plastic. The rolled, viscid sheets are exposed to the air, and when a certain degree of hardness is attained they are warmed and subjected to powerful pressure. This is done because, up to a certain point, the valuable properties of celluloid are improved in proportion to the pressure applied. The press plates are arranged as follows: first an iron plate, on this a zinc plate, and on the latter the sheet of celluloid to be pressed, this being covered with a zinc plate topped by one of iron. Of course a number of these sets of plates can be placed one above another.

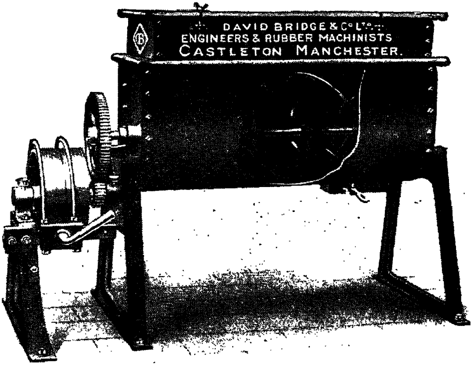


FIG. 25.—Horizontal Mixing Machine. David Bridge & Co., Ltd.

This ether process is only suitable for sheets or rods of moderate thickness, since a sheet two-fifths of an inch requires ten days to harden.

Magnus used Schering's collodion wool to some extent, and also imported pyroxylin, the latter being—in accordance with the law—carried in a wet, compressed state

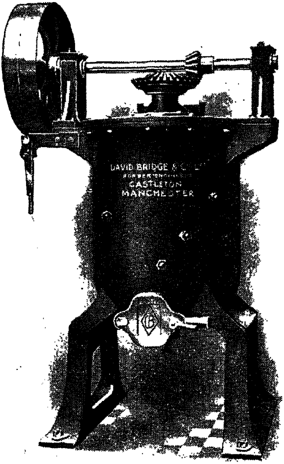


FIG. 26.—Vertical Mixing Machine. David Bridge & Co., Ltd.

(minimum water-content, 25 per cent.), and therefore having to be dried before use. So far as is known, the drying process, in the Magnus works, was performed on hot iron plates: this of course necessitating extreme care, and the employment of a temperature not exceeding 60–70° C.

The imported pressed material cannot be dried direct, as in its tangled condition it would greatly retard the solvent action of the ether and camphor. On this account it must, therefore, be pulled apart before drying.

To obtain good celluloid by the ether process it is also highly important that the cotton should be dry and perfectly free from acid, otherwise the celluloid is cloudy.

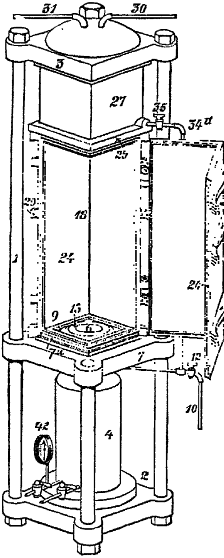


Fig. 27.—France's Drying Apparatus.

Preparation with a Solution of Camphor and Wood Spirit.—The gun-cotton, after being pulped with water, is treated with a mixture of camphor and wood spirit (methyl alcohol), the principle of the method being identical with that of Magnus. The crude celluloid is also dried in the same way as in the Magnus process.

An essential preliminary to success in carrying out the process is the removal of moisture; and for effecting this

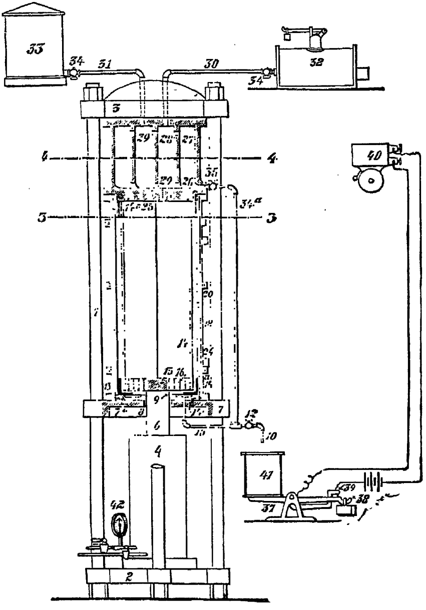


FIG. 28.—France's Drying Apparatus.

purpose J. R. France, of New York, has patented a process,* based on the application of hydraulic pressure to remove water, efficiently and cheaply, from large quantities of nitro-cellulose pulp, without risk of explosion.

* Eng. Pat. 17,692. Dec. 4, 1888.

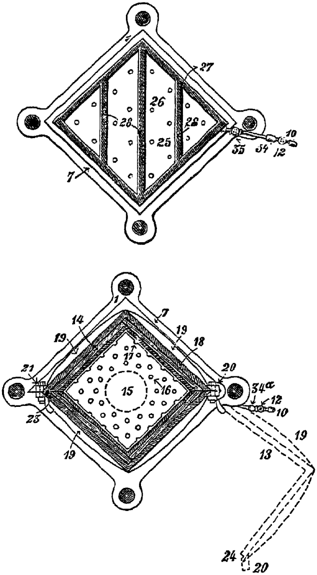
The extremely sensitive nature of the nitro-celluloses, especially their tendency to explode under pressure when in a dry state, renders the removal of the moisture difficult and dangerous. The method proposed for overcoming these defects is illustrated in Figs. 27–33.

Fig. 27 is a perspective view of the apparatus, but without the cage, which has been removed. Fig. 28 is a vertical section, with the cage shown in position.

Fig. 29 is an enlarged horizontal section along the line 3–3 of Fig. 28, whilst Fig. 30 is a similar section along the line 4–4 of Fig. 28.

The press chamber, of suitable construction, is mounted on the base plate, 2, and terminates at the top in a dome or press plate, 3; 4 is the cylinder and 6 the plunger of the hydraulic press, the plunger passing through the opening, 8, of the lower press plate. This plate carries a plate, 7*a*, fitted with a flange, 13, and a well, 9, forming the connection with the press chamber or cage and fitted with a discharge pipe, 10. The flange, 13, supports the lower edge of the cage or press chamber, 14, which is made up of sections, as shown in Figs. 31–33. The cage can be taken apart at the opposite ends, so as to render the interior accessible. One half of the cage is fitted with a rib, 14*a*, and inward flange, 14*b*, which fits against the inner surface of the cage. Above is a second rib, 14*c*, which can be either detachable or made in one piece with the other half of the cage. Inside is mounted a false bottom, 15, which fits easily, resting on the flange, 14*b*. It is perforated with holes, 16, and provided with channels, 17, round the outside. To facilitate handling, the cage is preferably made of wood, lined with zinc. Inside the frame, 1, of the press, and over the plate, 7, is a press chamber, 18, which is divided corner-wise, the two halves being connected together by hinges. When this chamber is closed, the sides surround the flange, 13, of plate, 7*a*. The outside of the chamber is provided with ribs, 19, and sockets, 20, to receive the bolts, 21, for closing the chamber. The bolts carry wing nuts, by means of which the joints can be tightly closed, the said joints being lined with strips of packing material, 23, in the grooves, 24. The press chamber encloses the cage, on which rests the flange, 13, of the plate 7*a*.

At the top of the press is a strong transverse wall, 25,



FIGS. 29 and 30.—France's Drying Apparatus.

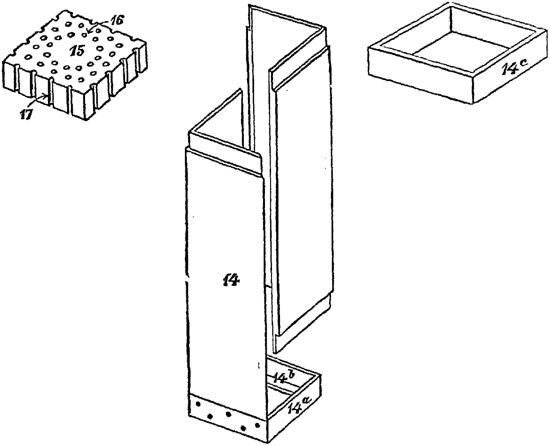
forming the press head. This wall is pierced with holes, 26, extending to an upper chamber, 27, divided by partitions, 28, provided with openings, 29, above and below. In connection with these two chambers are two pipes, 30 and 31, each provided with a tap, 34, and leading to an air compressor, 32, and an alcohol tank, 33, respectively. A pipe, 34*a*, that can be closed by means of a tap, 35, leads from the bottom of the chamber, 27, to the outlet pipe, 10.

On a level with the press is arranged a special form of weighing machine, the object of which will be explained later. If necessary, electric contacts, 38 and 39 can be provided on the beam of the machine and connected by wires with the bell, 40.

The apparatus is employed in the following manner. The nitro-cellulose coming from the washing tank is placed in a hydro-extractor similar to Fig. 18, but with a perforated cage, which is kept running until the pulp contains about its own weight of water. The mass is then taken out and made up into lumps weighing about 2 lb. each. A piece of muslin having been placed on the false bottom, one of the lumps of nitro-cellulose is laid on it and covered with a second layer of muslin. On this again is laid another lump of nitro-cellulose, and so on until the cage is full. The cage being inserted in the press chamber, the latter is fastened up, and the hydraulic press set in motion, the plunger rising and lifting the false bottom, 15, thus pressing the nitro-cellulose between the latter and the press head, 25. The pressure is raised to about 400 lb. per square inch, and this is maintained for an hour, during which time the expressed water runs down through the holes, 16, and channels, 17, of the false bottom into the well, 9, of the plate 7*a*, and away through the pipe, 10, whilst the water forced upward through the cross wall, 25, is drawn off through the pipe, 34*a*, to the pipe, 10*a*.

After the pulp has been pressed for about an hour, the tap, 34, is opened to admit air from the compressor, 32, this air penetrating the pulp and driving out most of the residual water therein. The compressed air is admitted for some little time after the water has ceased to flow, and then the tap is turned off and 90 per cent. alcohol is admitted to the chamber, 27, from the alcohol tank, 33, by opening the tap, 31. From this chamber the alcohol trickles down by gravitation through the cross wall, 26, and through the nitro-cellulose pulp, driving before it the traces of the heavier liquid, water, still left therein.

Practical experience with this apparatus has shown that about 30 per cent. of the water is expelled from the nitro-cellulose by the pressure employed, and a further 20 per cent. by the subsequent use of compressed air, so that about half the original quantity of water is left in the mass. The initial weight of water being known, the degree of drying obtained can be easily ascertained by collecting the effluent water in a vessel, 41, placed on a suitably counterpoised balance, 37. When the ringing of the electric bell, 40, indicates that sufficient water has been collected in the vessel, 41, the tap admitting the alcohol is closed and the vessel, 41, is replaced by another to receive the mixture of alcohol, which afterwards drains



Figs. 31-33.—France's Drying Apparatus.

away from the nitro-cellulose which can be distilled for the recovery of the alcohol. The compressed air tap is turned on again and the alcohol expelled until the nitro-cellulose contains 40 to 50 per cent. of its own weight of that liquid, whereupon the air supply is shut off, the press plunger is lowered and the press chamber opened. The cage now contains the nitro-cellulose or pyroxylin in compact layers, separated by the sheets of muslin, and therefore easily detachable. The amount of camphor necessary to fully convert the nitro-cellulose or pyroxylin into celluloid is now placed, along with the colouring matters and pigments, between the several layers of material, which are next piled up in zinc-lined chests and covered up tightly, to be stored until they can be rolled in the usual way.

To enable the pressure in the apparatus to be regulated according to requirements, a pressure gauge, 42, is mounted on the hydraulic cylinder.

The apparatus and method possess the following advantages. 1. The rapid expulsion of water from the pyroxylin, thus enabling a large quantity to be dealt with daily at a low cost. 2. Uniform distribution of the solvent, so that all parts are impregnated with alcohol, thus facilitating the further treatment with solvents. 3. Absence of danger in the drying process, the pressure applied to the pulp being low, and the pulp itself remaining moist throughout. The method is rapid, simple, reliable and cheap in operation, the alcohol remaining in the nitro-cellulose, and afterwards combining with the camphor, can be recovered by distillation.

CHAPTER IV

MANUFACTURE OF ARTIFICIAL SILK (LUSTRE-CELLULOSE, LUSTRE-CELLULOSE GLANZSTOFFE, FIL BRILLIANT)

WITHIN a comparatively short space of time an entirely new industry has been evolved and become of considerable importance, that is, the manufacture of artificial textile fibres resembling silk from solutions of cellulose.

The different processes are reviewed in a very comprehensive paper by E. Bronnert (*Bull. Soc. Ind. Mulhouse*, May–June, 1900, p. 177, also *Rev. Mat. Col.*, Sept. 1900, p. 267), an abstract of which will be found in the *Journal of the Society of Chemical Industry*, 1900, p. 819. A long series of articles by Joseph Foltzer in the *Textile Manufacturer*, vols. 37 to 40, and also *Artificial Silk: its Production, Properties, and Applications*, by Carl Suvern, Berlin 1900, J. Springer, may also be consulted.

The methods of manufacturing artificial silk from cellulose are grouped by Bronnert into four classes:—

1. Artificial silk obtained from the nitro-celluloses. "Lustre-cotton," "Glanzstoffe," "Fil brilliant."
2. Lustre-cellulose from a solution of cellulose in cuprammonium hydroxide.
3. Lustre-cellulose from a solution of cellulose in zinc chloride solution.
4. "Viscose" silks from cellulose xanthate.

The possibility of forming an artificial fibre from a fluid, just as a silkworm produces silk, first occurred to Réaumer in 1734, although he made no practical attempt to realize this desire, and it was not till more than a hundred years later that Andemars of Lausanne took out the first patent for this purpose (Eng. Pat. No. 283, Feb. 6, 1885).

The production of artificial fibres was first practically applied to the manufacture of electric-light filaments for obtaining which processes were invented and patented by Swinburne (*Electrician,* 1887, p. 286), Crookes, Weston (Eng. Pat. 22,866, Sept. 12, 1882), Swan (Eng. Pat. 16,178, April 28, 1884), and Wynne and Powell (Eng. Pat. 16,805, Dec. 22, 1884).

Wynne and Powell's patent consisted in dissolving cellulose in a solution of zinc chloride, iodide, or bromide, or in bismuth chloride or bromide, or a mixture of any of these, and precipitating it in the form of a filament by forcing it through a small orifice, or by rolling it between grooved rollers into a suitable setting liquid, such as alcohol, or ether, or the vapours of these liquids.

The first process for the manufacture of artificial fibres suitable for textile purposes was however that patented by Comte Hilary de Chardonnet, who employed solutions of nitro-cellulose for this purpose, and produced a very beautiful silky filament which was made on a large scale at Près de Vaux, near Besançon, Fismes, in Northern France, and at Walston in England. Chardonnet took out several patents for methods of manufacturing artificial silk, and the apparatus to be used therefor (Ger. Pats. 38,368, 1885; 46,125, 1888; 56,331 and 56,655, 1890; 81,599, 1893; French Pat. 231,230, 1893; Eng. Pats. 2211, Feb. 15, 1886; 5270, April, 9, 1888; 1656, Jan. 30, 1890; 19,560, 1891; 24,638, Dec. 21, 1893). The material employed by Chardonnet consisted of a solution of pyroxylin in ether-alcohol with the addition of a reducing metallic protochloride, and a small quantity of an oxidizable organic base, the formula being:—

Pyroxylin	100 grams.
Ferrous, chromous, manganous, or stannous chloride	10–20 grams.
Quinine, aniline, or rosaniline	0·2 gram.
Alcohol, 60 ; Ether, 40	2–5 litres.

—the pyroxylin being dissolved in the greater part of the alcohol-ether mixture, while the rest was employed to dissolve the metallic protochloride, the organic base, and the colouring matter, the two solutions being afterwards united. When this liquid in a warm state is forced through a fine nozzle surrounded by a cooling liquid, the superficial portion of the thin stream of collodion sets immediately, and thereby forms a solid thread. This thread is composed of an external, almost solid tube, enclosing an internal fluid column. The threads can thus be drawn out still finer in the air and resemble silk in their lustre.

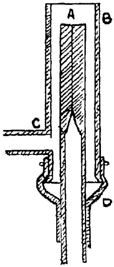


FIG. 34.—Spinnaret for Chardonnet's Apparatus.

The apparatus described by Chardonnet in Eng. Pat. 1656, 1890, shown in Figs. 34–36, consists essentially of the appliance for forming the filament from the liquid nitro-cellulose and spinning the fibre thus produced. The liquid is forced by a pressure of 10 to 12 atmospheres through capillary glass tubes, Fig. 34 and Fig. 35, each of which is surrounded by a tube, K, filled with cold water which is for cooling purposes. These spinning organs are fitted to a main tube, B, which is enclosed by two channels, C, through which water is also kept circulating. The working orifice of each spinning organ is surrounded by a pair of tongs with a light grip made of two flat springs, and all the tongs have imparted to them, through bell-crank levers, *o*, and bent arms, *p.p.*, a rising and falling swing motion from the spinning organs to the bobbins or reels, in such a manner that newly

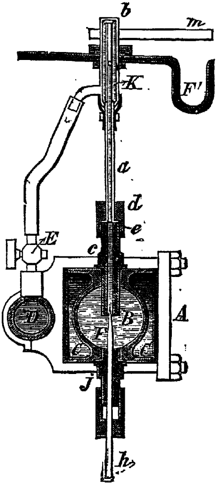


FIG. 35.—Chardonnet's Apparatus.

formed threads, just running over the edge of the spinning organ, or thick, easily breaking threads, stick to the tongs and are conducted to bobbins, whereas the tongs rise and fall empty so long as the threads do not break in spinning. A rotary brush, H, cleans the tongs on reaching the upper limit of motion. The spindles, S, of the bobbins, R, for winding the silk are mounted on loose cheeks, P, of the revolving shaft, O, and carry small rollers, V, which make contact with the periphery of cams, Q, mounted on the shaft, with the result that all the bobbins turn simultaneously and the cheeks also are

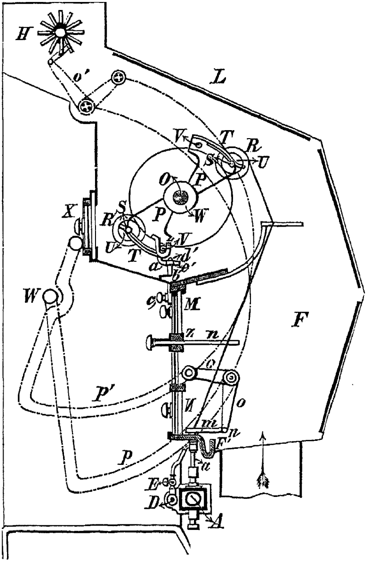


FIG. 36.—Chardonnet's Artificial Silk Apparatus.

moved simultaneously for the purpose of replacing the full bobbins by empty ones. The machine is enclosed in a casing, traversed by a current of warm air to remove the vapours of ether and alcohol, and convey them, for purposes of recovery, through a series of condensers, the first of which contains a concentrated solution of sodium carbonate, the second and third being charged with concentrated sulphuric acid. The bulk of the alcohol and ether settles down on the sodium carbonate solution, whilst the remainder is absorbed by the sulphuric acid.

The filaments first produced were of course exceedingly inflammable and suffered from several other defects, such as brittleness, etc. In order to obviate the first-mentioned defect, Chardonnet states in his patent (Eng. Pat. 2211, 1886) that the material can be rendered incombustible by a mixture of glycerine, gelatine and sugar.

The denitration of the fibre soon, however, followed, the first denitrating agent used by Chardonnet being dilute nitric acid, sp. gr. 1·32 (Eng. Pat. 5270, 1888) with which the material was treated at 30° to 40° C. for two to twenty-four hours according to the thickness of the threads. The action of the acid is, however, partial, the product still containing 6 to 6½ per cent. of nitrogen.

The progress of denitration can be followed by analysis, using the Schloesing method, in which, by the action of hydrochloric acid and ferrous chloride, nitric oxide is liberated, or more simply by solution tests with a solvent such as acetone or ether-alcohol which dissolves the ordinary pyroxylin but not the denitrated product, so that when denitration is completed the material becomes insoluble in these solvents, whereupon the fibre is washed and dried in a current of warm air.

It was soon found that other substances were more suitable for denitrating than dilute nitric acid. Various reducing organic substances and even pure water will denitrate pyroxylin although to a limited extent. At temperature above 15°–20° C. alcohol acts rapidly, hence in using this liquid for making solutions of pyroxylin care should be taken that the temperature is kept low.

Cuprous compounds are excellent denitrating agents, recent experiments having shown that in acid or alkaline solutions, or even in neutral solutions in presence of an alkaline chloride, complete denitration can be effected. Denitrating solutions can be prepared in various ways, such, for instance, as dissolving cuprous chloride in solutions of alkaline chlorides, *e. g.* sodium chloride and warming the nitro-cellulose in this. Typical proportions are 2½ to 6 parts of cuprous chloride, 20 to 50 parts of sodium chloride, dissolved in sufficient water to prevent the salts crystallizing out, and the treatment may be at temperatures between 25° and 100° C.

Ferrous chloride was recommended by Béchamp, ferrous chloride in alcohol is included in Chardonnet's addition to French Pat. 231,230, 1893, formaldehyde by Knofler (Ger. Pat. 88,556, March 28, 1894) and sulphocarbonates.

The most suitable agents, however, are the sulphydrates which have superseded all others. The different sulphydrates differ in their behaviour, but sodium and calcium sulphydrates are mostly employed, the latter being made from alkali waste at Besançon. Chardonnet also used a mixture of sodium monosulphide and ammonium sulphate, calcium monosulphide, made by heating plaster of Paris with charcoal, or the sulphydrates of the same (Eng. Pat. 24,638, 1893).

The denitration with these reagents is almost complete, a sample of "Lehner" silk, presently to be described, having been found by Cross and Bevan * to contain only 0·19 per cent. of nitrogen.

The denitration treatment, besides reducing the inflammability, adds considerably to the value of the fibre, rendering it softer, more supple, and more lustrous. The fibres are absolutely white and take basic dyes readily without a mordant, yielding extremely brilliant tints. The specific gravity of the thread is 1·5 to 1·55 and a thread of 100 derniers shows a tensile strength of 120 grams with an elasticity of 8 to 12 per cent.

The following table by Bronnert shows the effect of denitration on nitro-cellulose fibres.

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* *Journ. Soc. Chem. Indt.*, 1896, p. 317.

	TENACITY.	ELASTICITY (stretch).
	Weight in grammes required to break the thread.	Per cent.
Nitro-cellulose. (Chardonnet : Ger. Pat. 81,599)	150	23
The same after denitration	110	8
Denitrated fibre, moistened with water.	25	
Nitro-cellulose. (Bronnert : Ger. Pat. 93,009)	125	28
The same after denitration	115	13
Denitrated fibre, moistened with water.	32	—
Natural silk	300	18

The numbers are taken for thread of 100 derniers (450 metres of 0·05 grammes = 1 dernier).

The following table by C. Hassac* will also be of interest.

	Moisture.			No. of fibres to 1 sq. mm.		Tensile strength. Kg. per sq. mm.		Extension.
	Air dry.	Saturated.	Sp. gr.	Wet.	Dry.	Wet.	Dry.	Per cent.
Real silk .	8·71	20·11	1·36	9710	9710	37·0	37·0	21·6
1. Chardonnet	11·11	27·46	1·52	640	1135	2·2	12·0	8·0
2. Fismes .	10·92	27·12	1·52	370	656	1·6	7·8	11·6
3. Walston .	11·32	28·94	1·53	683	1620	1·0	22·3	7·9
4. Lehner .	10·45	26·45	1·51	413	1180	1·5	16·9	7·5
5. Cellulose .	9·20	23·08	1·50	742	1550	3·2	19·1	12·5
6. Gelatine .	13·98	45·56	1·37	265	945	nil.	6·6	3·8

It will be seen from the above tables how much weaker is the artificial silk than the natural product, and also the profound influence which water has upon this factor.

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* *Oest. Chem. Zeit.* 1900, pp. 235, 267 ; *Journ. Soc. Chem. Indt.*, 1900, 531.

After the denitration process was introduced, the use of the reducing salts and organic bases was discontinued, the solution containing nitro-cellulose only. The methods for making it, according to Foltzer, being as follows:—4 kilos (8·8 lb.) of cotton, steeped in 35 litres (7·7 gals.) of a mixture of nitric acid, sp. gr. 1·52, and sulphuric acid, sp. gr. 1·84, for four to six hours, excess of acid pressed out and the nitro-cotton washed with water till free from acid. The product is pressed in hydraulic presses and then contains 36 per cent. of water. Without drying it is dissolved in the proportion of 22 kilos (48½ lb.) in 100 litres (22 gals.) of a mixture of equal volumes of ether and alcohol, it is filtered by pressure through carded cotton and stored in large reservoirs ready for the machine. A solution which has been "aged" for a few days has a lower viscosity, and yields a better quality of silk. Alternative quantities are pyroxylin, 5 kilos (11 lb.), rectified ether at 65°, 36 litres (7·9 gals.) and alcohol at 95°, 64 litres (14 gals.).

Chardonnet in his Eng. Pat. 24,638 gives the proportions as 1 kilo of wood-pulp or cotton, soaked twelve to twenty-four hours in a mixture of nine litres of nitric acid of density 1·3 and fifteen litres of sulphuric acid of density 1·835, and mentions that this is a special hydrate which must not be dried previously to dissolving as otherwise it is spoiled. He also states that by adding a few hundredths per cent. of any of the following substances the solution is made more fluid:—ether, ethyl and methyl hydrochlorate, the chlorides of magnesium, aluminium, manganese, tin, etc., acetic acid, aldehyde, acetone, carbon bisulphide, hydrochloric, nitric, or sulphuric acids.

Attempts to render the silk waterproof and thus improve its strength have proved a failure (French Pat. 259,422, Sept. 3, 1896, etc.) Strehlenert proposed to do this by treating the threads with formaldehyde (Eng. Pat. 22,540, 1896), but no success attended his efforts.

Other inventors have endeavoured to improve on Chardonnet's methods, but with the exception of the processes of Lehner, presently to be described, little real progress has been made.

Vivier dissolves gun-cotton or nitro-cellulose in the strongest acetic acid, with the addition of a little gelatine. The nitro-cellulose is obtained from the powdered fibres of black poplar or boxwood, nitrated by the usual method.

E. Breuer patented a process for producing coloured threads (or with metallic lustre) from collodion without spinning. A roller of metal or other solid material is coated, first with a layer of collodion, then with glue solution, then with more collodion, and so on alternately, until a certain desired thickness is attained. The roller prepared in this way is put in a screw-cutting lathe, in which the coatings are cut through spirally, furnishing a series of continuous threads which, after passing through warm water to dissolve the glue, are reeled on to bobbins.

According to H. de Parville collodion cotton is dissolved in a mixture of ether and alcohol, and the resulting solution is placed in a tinned copper vessel, in which a pressure of several atmospheres is applied by means of an air-pump. In the bottom of this vessel is a sloping surface in which are mounted a number of vertical glass tubes, terminating in fine nozzles. A second tube surrounds each of the first, and by means of suitable connections enables a slow circulation of water to be maintained round the tubes communicating with the vessel. Under the influence of the pressure the collodion gradually issues from the capillary openings of the tubes and solidifies immediately it comes in contact with the water. The threads are seized by an automatic reel and wound on to revolving bobbins. After denitrating, the threads being gelatinous, are easily impregnated with colouring or saline matters, are no longer explosive and can be rendered incombustible by passing them through a solution of ammonium phosphate.

F. Lehner (Eng. Pat. 11,831, July 11, 1891) prepared at Glattburg, near Zürich, a nitro-cellulose by first treating satin paper, cotton, or spinning waste, or other forms of cellulose, with an ammonial solution of copper oxide

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(copper sulphate, 10 parts, ammonia, sp. gr. 0·975, 100 parts) for about fifteen minutes; the proportions being about 10 parts of cellulose material to 12 parts of the solution. In this liquid the fibres hydrate and swell to a considerable extent, which facilitates the subsequent nitration. The material is removed, thoroughly washed in a large volume of hot water, centrifuged, and then well dried. The cellulose thus treated is reduced to a flocculent condition and is added to a mixture of sulphuric acid (sp. gr. 1·84), 4 parts, and nitric acid (sp. gr. 1·4), 3 parts, which is warmed to 75° C. The cotton is well stirred in this, and after five minutes, the excess of acid is drained away, the cotton pressed, and then washed and dried in the usual manner. The nitro-cellulose is treated with wood spirit (9 : 1) and the mixture is shaken until it is practically all dissolved, whereupon it is set aside for a week in a cool place to clarify, the clear liquid being drawn off from the sediment. Two other solutions are also prepared: the one consisting of 500 parts of powdered copal or sandarac in 2400 parts of ether and 100 parts of linseed oil. The other made by dissolving 100 parts of sodium or ammonium acetate in 1000 parts of dilute spirit of wine. All these solutions are allowed to stand in order to allow the sediment to settle out or they are filtered to render them quite clear.

These three solutions are mixed together in such proportions that for each 1000 parts of nitro-cellulose there are 200 of copal or sandarac, 50 of linseed oil, and 100 to 200 of sodium or ammonium acetate.

Lehner soon, however, abandoned all additions to the nitro-cellulose with an improvement in the quality of the fibre. He used solutions of less strength than Chardonnet and by so doing obviated the necessity of using high pressures for forcing the liquid through the nozzles; a decided advantage. Lehner found that the fluidity of the collodion can be increased by the addition of small quantities of sulphuric and hydrochloric acids (Ger. Pat. 58,508; Eng. Pat. 22,736, Dec. 10, 1892) and made use of these for lowering the viscosities of the solutions.

Chardonnet also found (French Pat. 231,230) that aldehyde, sulphovinic acid, and aluminium chloride have the same effect, which, however, is not so marked on the concentrated solutions he employed.

Apparatus for spinning the nitro-cellulose is described in both Lehner's English patents, the one shown at Fig. 37 being illustrated in patent 22,736 of 1902. The solution is allowed to flow from a reservoir, A, to a series of bent glass tubes which are tapered at the open ends to form fine nozzles. These tubes are enclosed in a tank, G, which contains the solidifying liquid being separated by the partitions, *g*. The filaments formed by the issuing solutions, after solidification, are passed through rotating tubes, O, which impart to them a false twist, while cotton from a spool, P, can be run in association with it. The filaments pass backwards and forwards through the drying chamber, Q, which is heated by steam or hot water, and the vapours are conveyed by the pipe, *l*, to a condensing plant where they are recovered. The dried filaments pass over the roller, J, which is partly immersed in a denitrating liquid, and then between drawing rollers, T, to a spinning apparatus, *x′*, and then through fliers to spools. The revolving tubes *o* and rollers, T, are operated from a shaft,

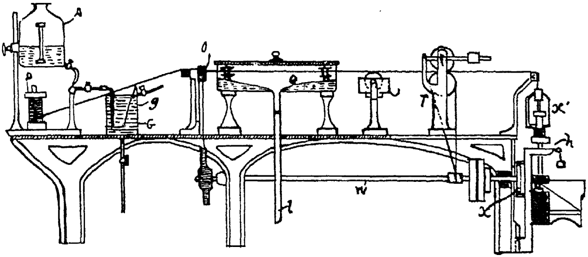


FIG. 37.—Lehner's Artificial Silk Apparatus.

W, while the alternating up-and-down motion of the frame, *h*, and spools is developed by an eccentric, X.

Bronnert found that alcoholic solutions of a number of inorganic and organic substances dissolve the lower cellulose nitrates (Ger. Pat. 93,009, Nov. 19, 1895; also Bronnert and Schlumberger, Eng. Pat. 6858, March 28, 1896) including oxalic, citric, tartaric and levulic acids, salts of these acids, or of hydrochloric or alkylsulphuric acids with alkalies, alkaline earths, aluminium and zinc, and ethers of the said acids with mono- or poly-atomic alcohols. The most suitable of these compounds is calcium-chloride, the most efficient proportion being one molecule of $CaCl_2$ to one molecule of tetranitrate, the maximum fluidity of this solution being attained by half-an-hour's heating at 60° to 70° C. (U.S. Pat. 573,132, Dec. 15, 1896).

Lustre-silk, obtained by spinning a solution of cellulose in cuprammonium hydroxide, is made by the Vereinigte Glanzstoff-Fabriken, Aachen, under several patents which were granted to H. Pauly (Ger. Pat. 98,642, 1897; Eng. Pat. 28,631, 1897), Fremery and Urban (French Pats. 286,692 and 286,726, 1899; Ger. Pat. 111,313, 1899), E. Bronnert (Eng. Pats. 13,331 and 18,884, 1889) and Consort. mulhousien pour la fabrikation de fils brilliants (Eng. Pat. 13,331, 1899).

The first patent was granted to Despeisses (French Pat. 203,741, 1890) who soon afterwards died, the method being developed by Pauly and subsequently by the other workers, the material usually being referred to as Pauly silk.

The chief difficulty encountered was that of preparing a solution of sufficient concentration, which was overcome by first converting the cellulose into a "hydrate," *i.e.* mercerising with strong caustic-soda solution and with this product it was possible to obtain sufficiently concentrated solutions. The filaments retain a portion of copper as hydrate, which is removed by passing them through a solution of acetic acid.

Lustre-cellulose prepared from a solution of cellulose in concentrated solution of zinc-chloride was used by Wynne and Powell in the manufacture of electric-light filaments (Eng. Pat. 16,805, 1884). More recently it has been employed for the production of textile fibres. W. P. Draper and H. K. Tompkins were granted a patent (Eng. Pat. 17,901, 1897) for the manufacture of such a fibre, the liquid being forced through capillary tubes into alcohol or acetone which dissolves the zinc chloride and precipitate the cellulose. Bronnert (Eng. Pat. 18,260, Sept. 9, 1889; U.S. Pat. 646,799, 1900) improved on this process by the preliminary treatment of the cellulose with caustic-soda solution—the mercerisation process—which then allowed the solution to take place in the cold, and thus did away with the long-continued digestion under heat which had been the cause of hydrolysis and weakening of the fibres.

The preparation of a compound of cellulose known as the thiocarbonate, xanthate, or "viscose," was the outcome of the researches of Messrs. Cross, Bevan and Beadle. The patent taken out by them (Eng. Pat. 8700, May 7, 1892, also 4713, 1896; Ger. Pats. 70,999, 1893 and 92,590, 1896) relates to a method of dissolving cellulose consisting in impregnating the material with a fifteen per cent. solution of caustic soda or potash, expelling the excess by centrifuging or pressing, and exposing the alkali cellulose, which will contain 40 to 50 per cent. of alkali, to the action of carbon bisulphide in a closed vessel at ordinary temperature. After several hours the material is converted into a gelatinous mass which can be diluted with water, forming a yellow solution. This solution after a time deposits compact gelatinous cellulose, which occurs also by heating at 80° to 100° C. or on treatment with an oxidizing agent. This solution can be spun in a similar manner to the other cellulose solutions yielding a fine lustrous silk which is now made on a very large scale, the raw material being purified wood-pulp.

More recently patents have been taken out by C. H. Stearn for the spinning of artificial silk from "viscose" (Eng. Pat. 1022, Jan. 13, 1898; Ger. Pat. 108,511, 1898), a solution being forced through orifices into a 17 to 20 per cent. solution of ammonium chloride, which sets it to a jelly, and afterwards the fibre is purified by passing it through solutions of sodium carbonate, hypochlorite and hydrochloric acid for bleaching purposes; finally it is washed with water and dried.

P. Krais and the Bradford Dyers Association, Ltd., in their patent specification (Eng. Pat. 18,742, 1904) state that in the treatment of fabrics for the preservation of the "Schreiner finish," which is imparted by heavy fluted rollers, the usual solvents for pyroxylin are unsuitable, the ether-alcohol mixture owing to the vapours evolved being explosive and unhealthy, while the odour of amyl-acetate clings to the fabric even after prolonged drying. They therefore claim the use of amyl-formate as a solvent for pyroxylin to be used for this purpose. Amyl-formate boils at a temperature of about 15° C. lower than amyl-acetate and leaves no objectionable odour behind. The solutions in this solvent are also more fluid than those of amyl-acetate, which is a decided advantage for spraying purposes. A five per cent. solution of pyroxylin is suitable for the purpose, being sprayed twice on the fabric after "Schreinering."

A practically inodorous mixture can also be prepared by using benzoyl-benzoate (W. G. Lindsay, U.S. Pat. 961,360, 1910).

CHAPTER V

PROPERTIES OF CELLULOID

CRUDE celluloid, free from all additions of colouring matter, body colours, or other substances designed for the production of special effects, is nearly colourless or faintly yellow, and in thin layers is as clear as glass, transparent to translucent, very elastic, hard, solid, nearly unbreakable, and can be cut with a knife or shears. It can be made harder or softer by suitable additions, though all attempts to render it permanently soft and plastic like gutta-percha have failed; specific gravity 1·25 to 1·45. Contrary to earlier statements, celluloid is not electrified by friction. Celluloid has a faint odour of camphor, this odour, which is not disagreeable, becoming stronger when the mass is rubbed, thus forming a means of identifying celluloid. Heated to 90° to 125° C. it becomes plastic, and in this state can be moulded into any desired shape. Separate pieces will coalesce on mere contact when warmed. At about 140° C. celluloid suddenly loses its colour and transparency, and at about 5° higher decomposes with liberation of pungent, readily inflammable vapours.

Warm, plastic celluloid forms an excellent cement for metals, a property of considerable utility in the production of inlaid work.

Celluloid softens in warm water, becomes flexible and somewhat plastic, so that it can be easily moulded to any desired shape. This property, also, is very valuable in the manufacture of celluloid articles, since the moulding process is greatly facilitated, loss of material prevented and time saved.

When ignited, celluloid burns with a smoky flame much more rapidly than sealing wax, an odour of camphor being at the same time perceived. When the flame is blown out shortly after ignition, the mass continues to glow briskly and gives off thick fumes of camphor that will soon fill a small room. Undoubtedly the gun-cotton burns in this case at the expense of the oxygen which it contains, but the temperature is not sufficiently high to ignite the camphor vapour. This behaviour indicates most clearly that celluloid is not a chemical combination of camphor and gun-cotton or collodion cotton, since it is characteristic of chemical compounds that the substances entering into combination cease to exist independently in the compound.

Celluloid can be ignited only by a naked light, and if heated in a vessel of any kind it simply decomposes, as already mentioned, at about 150° C., suddenly and completely, with the liberation of a large amount of smoke and, it is stated, with the formation of pyroxylin and camphoric aldehyde; at 195° it decomposes instantly, the nitro-cellulose burning and the camphor being vaporized. In no case, however, is there any approach to an explosion, for celluloid cannot be exploded either by pressure, shock, percussion, friction, heat, or any other means. Celluloid is no longer nitrated cotton, but a substance differing therefrom in all its properties.

The property of celluloid of softening in hot water enables it to be cut into sheets of any desired thickness, and also to attach itself, like putty, to wood, marble, etc.

If two surfaces of celluloid be coated with collodion and pressed together, they will unite firmly to form a solid whole. Thus two or more sheets of celluloid may be cemented to form a thicker sheet, or boxes, battery cells, etc., can be constructed from them.

Celluloid is insoluble in water, and on this account is suitable for making domestic articles, such as knife handles. Though it is not directly attacked by concentrated sulphuric acid, it gradually dissolves therein in the cold, a small piece entirely disappearing in about thirty-six hours. It also gradually dissolves in concentrated nitric acid, and in boiling caustic potash solution.

The tensile strength of celluloid is considerable. According to the results of a few tests, the elastic limit is about 200,000 to 240,000 lb. per square inch, that of iron being about a hundred and thirty times as great, and that of wood about seven times as great.

The elasticity is also high, as can be demonstrated by an easy experiment. The tip of a celluloid hairpin, for instance, can be bent round until the two ends meet, and back again until the ends meet at the opposite side; and this can be done any number of times, the pin retaining its original appearance when straightened out. To break off the tip it must be bent to and fro rapidly with considerable force. These simple tests clearly show the extreme pliability of celluloid. The substance can be stained any desired colour, the colouring matter not being absorbed merely superficially, but permeating the whole mass—as may be seen by examining fractured surfaces of celluloid articles. By means of suitable additions and treatment, celluloid can be made to imitate a great variety of materials, for which purpose it is extensively used. In all conditions its surface is extremely smooth and lustrous; it can be sawn, filed and turned in the lathe, and in general treated like horny materials.

Celluloid can be rolled, polished, pressed, cut and hammered, and can also be kneaded at a temperature of 145° C., so that, on occasion, it may be used in place of metals, stone, wood and wax.

The specific gravity of celluloid varies according to the degree of pressure it has been submitted to in the manufacture, the mean being 1·35.

CHAPTER VI

TREATMENT AND APPLICATION OF CELLULOID

CELLULOID is used for a great variety of purposes that are constantly being extended, there being now few if any industries in which this substance does not find employment in some form or other. In its natural conditions, without the addition of colouring matters or other adjuncts, celluloid is very extensively used, especially as a substitute for horn, tortoise-shell, coral, malachite, lapis-lazuli, marble, ebony, yellow or black amber, bronze articles, caoutchouc, ebonite, etc.; and, in fact, there is hardly a single substance known but that attempts have been made to imitate it with celluloid. For the above purposes it is used to a very large extent, and many articles of fancy ware, ornaments, etc., are now made of celluloid. In many other branches, too, celluloid has found application, such as for making artificial teeth, flexible mirrors, decorations in the greatest variety, spectacle frames, watch cases, buttons, pipe mouthpieces, cigar-holders, ash trays, soap boxes and trays, etc.

In fancy goods and hardware celluloid is used for making brooches, hairpins, bracelets, chains, earrings, crosses, medallions (either by itself or in combination with inlaid or riveted metals), imitation horn, tortoiseshell, coral, ivory, etc. It is also made into smooth, inlaid or stamped buttons, knife-handles, toothbrushes, prayer-book and album covers, cigarette cases, notebook covers, travelling cases, shoe eyelets, purses, pen and pencil cases, rulers, drumsticks, finger-stalls, serviette rings, cigar-holders, dolls' heads and bodies, mirror and picture frames, figures for games, stick, umbrella and whip handles (in a great variety of shapes and patterns which compete successfully with handles of other materials), billiard balls, chessman and other figures used in games, etc.

For fans, celluloid is a somewhat expensive material, but is nevertheless used.

Celluloid Industry.—Celluloid is used to a very large extent as a substitute for horn and hard rubber for making plain and fancy combs. Some of the larger firms laid down expensive plant for making toilet combs, and can turn them out at a price below that of the small maker who cannot afford such costly machinery. Celluloid combs are beautifully soft, elastic and durable, and share with tortoise-shell the advantage that, when broken, they can be repaired, becoming equal to new, by welding. Within the last few years celluloid balls, which are very elastic and in good demand, have been put on the market.

Makers of fancy wooden articles have successfully employed celluloid, which they use largely in different forms for covering and inlaying boxes and other fine work.

In the machinery and building trades, again, there is a large consumption of celluloid for emery discs, packing rings, tubes, valves, taps, pistons. It is used in coach-building for making axle bearings, since it is not corroded by oil and therefore forms also a good material for axle-box covers.

In railway work celluloid is used in the form of washers and rings for tightening up fishplates.

Since celluloid can be produced in discs or plates of any desired size, it is used as a stopping for flooring that is desired to be watertight, especially in ships and boats; in the former, indeed, it has also been proposed as an external coating to prevent the growth of parasites.

In dentistry the use of celluloid has attained considerable importance for the manufacture of roof plates.

Opticians employ celluloid for spectacle frames, lorgnettes, mounts for magnifying glasses and opera glasses. just the same as horn, tortoise-shell, or caoutchouc.

In brushmaking use is also made of celluloid to a considerable extent, since it possesses the great advantage over wood and other materials that it does not warp on wetting. Latterly also hogs' bristles have been replaced by stiff celluloid threads.

Art is also finding employment for celluloid, inasmuch as this substance—so far as experience goes—may be regarded as a durable ground for painting upon.

In medicine celluloid has been proposed, and used, as a material for surgical bandages, also for bottle-caps, and, in microscopic work, for section cutting.

Celluloid has, moreover, been used as a material for stamps and printing blocks, and proposals have recently been made to employ it as a substitute for type metal. In this latter connection, however, there is no practical experience at present available as to its utility. On the other hand, it has proved an admirable substitute for stiff collars and cuffs, especially for travellers and pedestrian tourists in summer, owing to its clean white appearance and its imperviousness to perspiration and wet. The celluloid used for this purpose looks like well-stiffened linen, is flexible, and can be worn for months, being easily cleaned with soap and water. It is also suitable for protective collars on uniforms and as a substitute for cloth facings that are exposed to much wear.

As a leather substitute celluloid finds application for coating harness, buckles, etc.

Being readily soluble in certain volatile solvents, and insensitive to moisture, celluloid has made its way into varnish making, especially for varnishes intended to protect metals from rust and oxidation. This same property is utilized in the manufacture of waterproof fabrics, in place of calico, for bookbinding; but celluloid is too combustible to be recommended for this purpose. It is extensively used in the form of a solution or "dope" for coating aeroplane wings, for which purpose it has been found very successful.

Thus we see that a material which, thirty years ago, was regarded with great suspicion and was denounced as inflammable and dangerous, has taken the premier place in many trades and industries; and since its price is now moderate, the sphere of its application will continue to increase—which is already shown by the innumerable patents taken out for its employment.

As already mentioned, the great plasticity of celluloid when in a warm state renders it very easy to mould or work it into various articles; while when cold it can be turned, bored, filed, etc., in precisely the same way as the ordinary materials worked by the turner. Even a temperature of 75° C. renders celluloid plastic enough to be moulded into any desired form in the press, though, as a rule, workers in celluloid heat it to about 120° C., at which temperature it is, of course, much more plastic than at a lower.

The matrices in which the pressing is done must have been warmed beforehand. The celluloid, warmed to 120° C., is placed in the matrix and subjected to considerable pressure, which is continued until the mould is cooled (cooling water is not always required), and the material is fixed in its new shape.

In cutting celluloid, and in all other operations where it has to be worked with iron tools and at high speed, it is advisable to allow drops of water to fall on to the point where the cut is being made. For articles that are to be beaten or pressed out, the celluloid is preferably warmed in water to 40° C., in order to prevent splitting and tearing. If the celluloid has become too brittle to work easily, it should be dipped in spirit of camphor for a short time.

Owing to the solubility of celluloid in various liquids, it can be easily cemented to other materials or upon other celluloid. An adhesive for this purpose is formed of a mixture of one part of shellac, one part of spirit of camphor, and three to four parts of alcohol. In addition to collodion, pure, finely shredded celluloid dissolved in absolute alcohol makes a good celluloid cement.

To facilitate the escape of camphor vapours from finished articles, these should not be stored in closed boxes or cases.

An important part in the working up of celluloid is played by the moulds, both those used for pressing the celluloid sheets and rods, and those in which celluloid is treated in a more or less plastic condition.

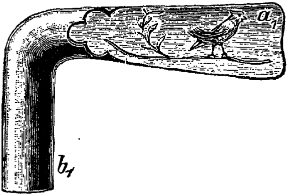


FIG. 38.—Umbrella Handle.

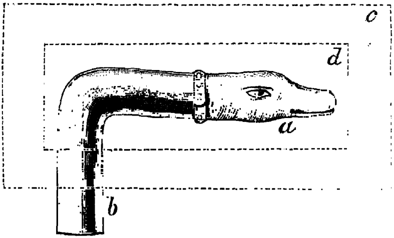


FIG. 39.—Mould for Umbrella Handle.

These moulds are usually of metal (steel, brass, or similar alloys), contain all the variations of contour of the finished article, and are polished when necessary, so that no after treatment will be required. These moulds, which are more or less elaborate, according to the nature of the article, are expensive, and attempts have therefore been made to construct them of other materials. Mendelssöhn, of Leipzig, uses wooden moulds, which possess the great advantage that they can be employed for pressing or blowing celluloid without any previous warming, the wood being a bad conductor of heat and therefore not withdrawing heat from the celluloid. Figs. 38 and 39 represent specimens of pressed articles, while Fig. 40 is a longitudinal section of a wooden mould. To press or blow celluloid articles, especially handles for umbrellas, sticks, etc., without any previous warming of the moulds, block or rod celluloid, of suitable thickness, is immersed in boiling water until it is warmed to 100° C., and is then bent into a shape corresponding to that of the mould, *b*, as shown at *a* and *a′*. It is then placed quickly between the two halves of the mould, *c*. If the article is to be solid, the two halves of the mould are pressed together in a suitable manner. Hollow articles are made by admitting steam or other press fluid into the mould containing the (tubular) celluloid, thus forcing the latter into all the contours of the mould. In contrast to metal moulds, which have to be warmed up again each time they are used, wooden moulds can be employed again in quick succession without removing them out of the press, the low conductivity of wood preventing the celluloid from being robbed of the previously accumulated heat.

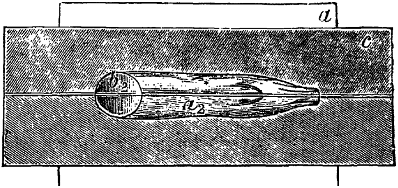


Fig. 40.—Section of Wooden Mould.

The wood used for moulds is moderately hard, such as oak, beech, etc.

According to R. Stübling, cheap and useful moulds can be made from wax models by the electro method, a coating of copper being deposited on the surface of the wax, the latter then removed by melting and replaced by molten alum. The copper deposit is strengthened by a coating of nickel, which is rubbed over with oil, a wax cast being then taken of each half, the outer side of the mould being backed with clay. These wax casts are rubbed over with graphite, to form a conducting surface, and a fresh electro is made, this being filled with plaster of Paris and employed as matrix for a mould of fusible metal.

For this purpose the celluloid is made up into sheets, one twenty-fifth to half an inch thick, and about 12 inches wide by 30 inches long; rods about 40 inches long are also used to some extent. The celluloid used is either perfectly transparent, yellowish and horny, or in the form of imitations of coral, malachite, amber and tortoise-shell. There are two methods of working:—

(*a*) *Working by the Cold Process.*—The sheets are cut up in suitable pieces with a circular saw, and the pieces worked to pattern with fret saw, graving tool, file, or turned on the lathe, to form brooches, earrings, pins, medallions, bracelets, etc., being finished by grinding them smooth with finely powdered pumice and fat, by means of quickly revolving wood discs covered with buckram or carpet fabric, and finally polishing with a buffing wheel and levigated chalk.

The majority of articles are then ready for piecing together and mounting, the various parts of a brooch, earring, etc., being screwed together, fitted with pin or hooks, packed, and sent out for sale.

To save material and time in the case of brooches or other articles representing twigs or sprays of coral, these are cut out of thin sheet material and finished on the flat as above, after which they are made soft and flexible by immersion in boiling water for a few seconds, and the leaves, coral twigs, etc., bent in various directions by hand. being set in their new position by rapid cooling in water. Were it not for the flexibility of the celluloid, such articles would consume fully three times as much material and time in the making. Similarly, bracelets are made of straight, flat strips, which, after being polished, are softened in hot water, bent round a circular block into the desired shape, and then cooled and dried.

(*b*) *Working by the Warm Process.*—This process entails the use of:—

1. Metallic heating plates, kept hot by means of petroleum, or gas flames, or preferably by steam.
2. Presses.
3. Moulds or matrices of steel or gun-metal.

The sheets of celluloid are softened on the hot plate, and cut into suitable small pieces with a knife. The pieces, rendered perfectly plastic by heating to a temperature of about 120° C., are next laid in the well-warmed moulds, and kept under a fairly powerful press until the mould has cooled somewhat, whereupon the article is taken out of the mould and cleaned, polished and mounted. Metal ornaments laid in the mould will incorporate with the celluloid thoroughly during pressing. Articles formed in this way lose their shape entirely when reheated; consequently this process is not adapted for the production of strips for bracelets, since the latter would lose the shape imparted in the press on being warmed in hot water for the purpose of shaping them to the arm as described under the cold process.

Celluloid Combs.—These combs are made in the same way as horn combs, so that any one accustomed to work in horn can make celluloid combs, provided he understands how to polish this material.

There is, however, one important particular in which the two processes differ, to the advantage of celluloid, namely, that the troublesome preliminary treatment necessary in the case of horn is dispensed with. The extent of this advantage can be realized by considering the various stages of making horn combs up to that of cutting the teeth. The hollow part of the horn has first to be cut crosswise into lengths, these in turn cut lengthwise, and each strip boiled in water for some time to soften the horn, after which they are fastened on the heating stick, held over a fire and kept turning, in order to heat them still further.

Next come the processes of spreading out flat, scraping to uniform thickness, pressing, splitting, smoothing in the press, etc., all of which are unnecessary in the case of celluloid. The combmaker buys his plates or sheets of the proper thickness, saws them into suitable sizes and smooths out any irregularities by warming the pieces under gentle pressure. Even in the cutting process celluloid presents several advantages over horn, the pieces of the latter having to be clamped on the slope and the saws accurately guided, in spite of which the horn frequently splinters or breaks, whereas none of these inconveniences arise with celluloid. The latter shares with tortoise-shell the useful property of being weldable when broken.

Cutting is effected by hand or machinery, just the same as with horn or ebonite, and the same processes are used in finishing. The combs are polished with pumice and tripoli powder, by means of sticks covered with woollen cloth. Water is allowed to drop on the comb, to keep it from getting too hot and softening, or decomposing and giving off fumes.

Fancy combs of celluloid are bent after softening them in hot water, though some makers bend them over a charcoal fire.

Cheaper combs are made in pairs, the hard-dried thick plates being warmed and the teeth cut in a stamping press. The combs made in this way, however, have merely plain, unornamented backs, and the teeth are devoid of taper; and even softening the plates in water before pressing in moulds, or hot-pressing soft, undried celluloid in moulds, will not give perfect combs. This disadvantage has been overcome by taking the fresh, plastic celluloid plates direct from the cutting machine, pressing them into the form of comb plates (tapered teeth and ornamented backs) in moulds, either in a cold or gently warmed state, and immediately cutting, filing, or stamping out the teeth, without drying the mass, which in this condition is easy to work, does not injure the tools, and gives a perfectly smooth-cut surface. The finished combs are then dried in a suitable apparatus to prevent the teeth warping; and this process enables combs of various shapes to be made. The comb and teeth dry quickly and hard, and become very strong.

Celluloid as a Basis for Artificial Teeth.

Teeth of bone, ivory and walrus tusks have been displaced by gold, platinum and palladium plates set with enamel teeth. Hard rubber has also been used, but is attended with numerous disadvantages, notably symptoms of mercurial poisoning; and traces of this metal have been discovered in the urine and saliva of persons using hard rubber teeth setting, which has also been known to give rise to disorders, such as salivation, diarrhœa, inflammation of the gums, etc., which disappeared when the rubber plates were discarded. The cause of the trouble was the vermilion used for colouring the plates; but no evils of this kind attend the use of celluloid plates, although these latter are sometimes coloured with vermilion, and it must therefore be assumed that the colouring matter is retained more tenaciously in the mass than is the case with rubber, the saliva being unable to dissolve it out of the celluloid.

Other advantages of celluloid include the possibility of colouring it in exact imitation of the gums, which could not be done with hard rubber. Celluloid is also easy and safe to work, whereas the vulcanizing autoclaves for hard rubber have repeatedly been known to explode.

Celluloid can be used in dentistry both for making the plates and also for entire sets of teeth. A solid mould (usually of gypsum) is made from a wax model, and into this mould the celluloid, in a softened, warm state, is pressed or injected. Various appliances have been devised for making celluloid teeth.

Jüterbogk's apparatus, which closely resembles the vulcanizing apparatus used for caoutchouc teeth, consists of a casing, on which is mounted the mortar-shaped steaming vessel containing the mould. The mould clamp is held in position by a device inside the steamer in such a manner that it cannot move when the clamping screw is being turned. The steamer is covered with a simple lid, provided with a hole for the passage of the clamping screw of the mould, and a fitting to hold the thermometer. The pressing temperature is 150° C., at which heat celluloid is plastic throughout its entire mass.

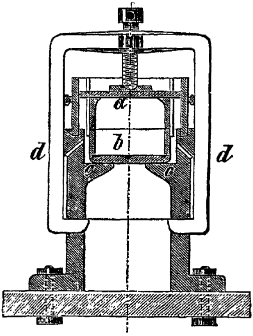
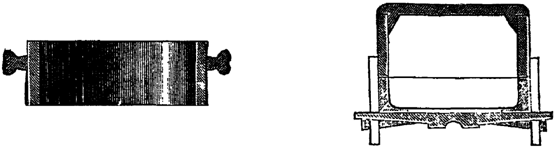


Fig. 41.—Hamecher's Apparatus.

Hamecher says of his apparatus for making artificial teeth plates that all the existing apparatus for treating celluloid for dental purposes have in common the features that the mould is arranged in a vessel or pan heated from without, the celluloid being rendered plastic in the mould and then pressed. His apparatus was based on the idea of avoiding the risk of explosions of the steaming vessel, and dispensing with a steamer by heating the mould itself. It was necessary to pay great attention to regulating the flame, in order that the same, however large, should not rise above a certain height, the level in all cases being below that of the celluloid to be pressed. This apparatus is shown as a vertical section in Fig. 41. A hollow cylinder, mounted on three symmetrically disposed feet, is provided internally with three projecting vertical and radial lugs, *c*, supporting the mould in such a position that the top of the lower half of the mould is on exactly the same level as the upper edge of the cylinder. In order to hold the upper half of the mould in exact vertical register with the lower half, the latter is provided with three wrought-iron guides, two of which are narrow and the third broad, and the upper half carries three guides accurately fitting into the others. The casing (Fig. 42), a cast-iron ring with two handles of wood, is high enough to overtop the open mould, and fits into an annular groove in the top of the cylinder, so as to form an extension of the latter. When the mould is in position the cover fits exactly into the casing. The flame is arranged so that the burner is outside the cylinder, and consequently an ample supply of oxygen is admitted. On the other hand, the flame would only reach the bottom of the mould were it not for the provision of a number of draught holes, *d*, sloping inward and upward through the wall of the cylinder, which they penetrate at a point



FIGS. 42 and 43.—Hamecher's Apparatus.

about half an inch below the upper edge of the top half of the mould, so as to permit the passage of the flame up to the level of the said holes. At the same time the whole of the space between the flame and the lid of the mould is warmed, and after about twenty-five to thirty minutes from the start the thermometer registers 150° C., the necessary temperature at which the mould is screwed down.

The *modus operandi* is as follows. A wax model is made of the teeth or plate, and a plaster cast taken of the model, the wax being melted out with hot water when the plaster has set hard. A piece of sheet celluloid the same length as the test plate is placed in the mould, which is then closed. To collect any celluloid escaping when pressure is applied, a channel about $\frac{1}{25}$ to $\frac{1}{12}$ of an inch deep is arranged, preferably in the top half of the mould, but not in any way connected with the model. When the mould and casing have been placed in position, the thermometer is inserted and the lamp lighted, care being taken that the flame is not too small, but large enough to cover the entire space under the mould. It often happens that the thermometer quickly indicates a temperature which, however, is not attained by the mould in less than twenty minutes; but this should not lead one into error. After a short time all disturbances will have ceased, the water vapour being expelled from the plaster, whereupon the thermometer will give the correct reading. The desired temperature (150° C.) will be attained sooner or later, according to the intensity of the flame, whereupon the mould may be screwed down, all that is necessary being to first extinguish the flame and remove the thermometer. It is necessary to put out the light, or the celluloid expressed from the mould may take fire. The screw is turned quickly, the upper surface of the mould cover being watched to see if it remains horizontal. If it is found to tilt the screw is reversed, the casing taken out of its groove and the mould pushed in the opposite direction so as to equalize the pressure.

When the celluloid offers too much resistance, the mould should be opened a little way (about $\frac{1}{8}$ inch) and left in that condition for one to three minutes before pressure is again applied. The hot plaster will by that time have warmed the celluloid sufficiently to make it much more plastic, as will be evident by the screw turning more easily. If the mould still does not close completely, it is left a few minutes longer and the screw again turned. About ten minutes after the mould has been closed up, the plastic mass will have begun to contract, the pressure will diminish and the molecules draw closer together. The mass hardens, and pressure is applied only at intervals (3 to 4 mins.), after which it becomes unnecessary to press any more.

If the apparatus is to be used again at once, the mould is wedged properly and lifted out of the apparatus. It is preferably left for half an hour after pressing, and then cooled rapidly by dipping in a pail of cold water, or holding it under a tap. When the outside is cold, the bottom is removed and the temperature of the plaster ascertained. If this is sufficiently low the cover is taken off, and the lower part of the mould is tapped with a hammer several times, causing the whole of the plaster to fall out, with the top half of the mould, whereupon the plaster is broken and the moulded article exposed. Any adherent particles of plaster are picked out with a knife, but it rarely happens that the article needs to be touched up with a file or graver, all that is necessary being to rub it over with fine sandpaper and polish with oil, soap and levigated chalk.

STAINED CELLULOID SHEETS AS A SUBSTITUTE FOR GLASS.

Thin celluloid sheets can be stained superficially, on one or both sides, by dipping them in a bath of coal-tar dye, prepared by pouring an alcoholic solution of the coal-tar dye into a bath of 99 per cent. spirit containing white shellac and sandarac, or some other resin. This bath is acidified with boric acid, and shortly before use a little ether or benzol is added, to accelerate the drying of the coloured layer on the surface of the celluloid.

The celluloid sheets are immersed for a short time merely, this being sufficient to mordant and colour the surface. The coloured layer dries very quickly. If only one side of the sheet is to be stained, the other is first coated with asphaltum in the usual manner. These coloured sheets are suitable for signals and identification devices, being unbreakable and the colours fast.

CELLULOID PRINTING BLOCKS AND STAMPS.

The reproduction of woodcuts by means of celluloid presents numerous advantages, the plasticity of this material enabling it to penetrate the minute depressions of the pattern block, and furnishing an accurate reproduction of the woodcut, even superior to electros, which, owing to the absence of the intervening layer of graphite, are not absolutely perfect. The method adopted is as follows. A cement cast is taken of the woodcut, this material being easily detachable without injuring the reproduction, and serving to replace gutta-percha. This cement casting is placed in contact with a softened sheet of celluloid in a hydraulic press, and in five to six minutes the celluloid will have been forced into even the finest parts of the mould. The entire operation takes only half an hour. The celluloid is superior in many respects to an electro block, as it stands the pressure better in quick-running presses, and is said to yield over 100,000 impressions.

Celluloid stamps are very elastic and durable, the wear being small; and they are superior to rubber stamps inasmuch as any kind of stamping ink can be used without risk of corrosion from the colouring matter. They are very easily made, a sentence set in type, or a mould (letters, pictures, ornamental devices, etc.) cut in wood, being laid on a flat surface, preferably of hard wood or stone, and covered with a moulding frame a little smaller than the mould, in order that the edges of the frame may fit closely. The inner sides of the frame slope inward, so as to support the plaster cast when the frame is raised; and the long sides are provided with recesses for the insertion of the lifting tool.

All parts of the mould that are to be covered with plaster are oiled with a small soft brush, so that even the spacing leads and quads are properly coated. The oil for this purpose is made by mixing 32 parts of bone oil, 32 parts of oil of turpentine, 1 of cotton-seed oil and 1 of white copal varnish slightly warm.

Finely ground, freshly burned stucco plaster is used for the casts, and this is made into a thick pulp with clean well-water in a suitable pail, the mixture being poured on to the surface of the mould so as to barely cover it. This is now worked into the lettering by means of a stiff brush, so as to fill up all the depressions in the mould, after which a fresh quantity of plaster is poured in until it begins to run over the edges of the frame, the surplus being brushed off with a straight edge after settling. In five minutes the plaster will have set hard enough for the frame and matrix to be taken off the mould by means of the lifting tools.

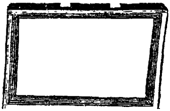


FIG. 44.—Mould Frame.

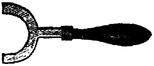


FIG. 45.—Lifting Tool.

A gentle tap on the forme holding the mould will loosen the plaster from the mould, when the frame and plaster cast can be lifted by means of the tool illustrated in Fig. 45, the points being inserted in the recesses in the frame (Fig. 44). A gentle tap on the frame will detach the plaster matrix, which can be transferred shortly after to a drying apparatus.

This consists of a strong sheet-iron stove, with a fire in the lower portion, so disposed that all parts of the plate supporting the drying frame are heated uniformly. The upper part of the stove is fitted with a drying rack, of one or two stages, the fresh matrices being placed on the lower stage, whilst the upper one is for final drying. The drying rack consists of an iron plate, from which project twelve to fifteen iron-wire arches, about an inch apart. The matrices are placed between these wires so that the fronts and backs are exposed to the ascending heat. To ensure uniform drying, the matrices have to be turned at frequent intervals, otherwise they would warp from uneven drying and break in the press. With a good fire a stove full of matrices will dry them in about four to six hours. If there are two stages, the matrices are taken off the bottom one at the end of that time, and placed on the upper rack, the other being recharged with a fresh supply. When the matrix has assumed a whitish yellow colour, and rings on being tapped on the back with the finger, it is properly dried. The slightest trace of moisture in the middle of the mass renders the matrix liable to break in the press, or to furnish a poor stamp.

The dried matrix is brushed over several times with a thin solution of shellac, to give it a smoother surface and greater durability, a point of considerable importance in the subsequent pressing.

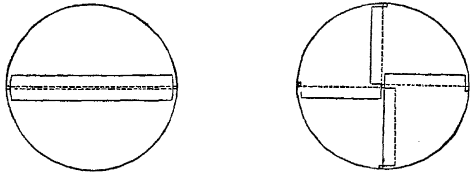
The matrix is now a yellowish-white block of varying thickness, containing an impression of the letters in their right order. The depth of the impression corresponds to the height of the original design on the type-block or woodcut, whilst the remainder should form a flat even surface if the stamp is to be of any use.

To prepare a stamp from this matrix, a sheet of celluloid is cut to the proper size, the piece being then placed in a water bath, at 70° C. exactly, for ten minutes, until the celluloid is thoroughly softened. Meanwhile, the press has been got ready, the mould placed on the loose table, the celluloid is taken out of the water, quickly laid on the matrix, and the table is pushed into the press, the latter being started at once. After being in the press five minutes the table is drawn out again, and the celluloid will be cold enough to be taken out of the mould without injury. It would be an improvement to jacket the press and raise it to the requisite temperature (70° C.) by means of steam or hot water. With this arrangement a number of moulds, containing the celluloid sheets, could be inserted into the space inside the press, and on attaining the proper temperature be pressed for five minutes and taken out again.

The softened celluloid is forced into all the depressions in the matrix, just the same as in making rubber stamps, so that the design appears in reversed, raised letters, etc., on the face of the celluloid. On cooling, the latter resumes its original hardness, and the plate can be glued or cemented on to the handle of the stamp.

Collapsible Seamless Vessels of Celluloid.—Collapsible tubes of celluloid are difficult to make, since the material cannot be brought into the form of a sufficiently thin, flexible and compressible tube. Vessels manufactured from thin sheet celluloid soon become brittle and inelastic, especially when they are kept in contact with hygroscopic substances, such as toothpaste, etc. To make these tubes and other hollow articles, a cylindrical incompressible core is dipped repeatedly into dissolved pyroxylin until sufficiently coated; the coating is dried, and is then drawn off the rigid core by the combined assistance of heat and moisture, which help it to come away easily. The material used (a solution of celluloid in amyl-acetate) is insensitive to the action of moisture, dilute acids and alkalis, whilst at the same time it is strong, very flexible and elastic, and does not lose these properties after being in contact with hygroscopic substances. The material is so thin that the tube will return to its original shape if pressed when empty, but will remain flat after being pressed when full. The core employed is a glass tube of the desired form and size, and provided at the lower end with a tapering screw neck. The finished tube is detached from the core by dipping it in water, or treating it with steam. The screw cap is made of aluminium or other metal. After filling, the open end of the tube is bent over and fixed with a metal clip.

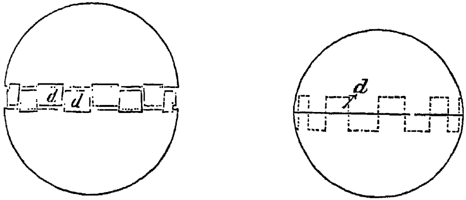
Making Celluloid Balls.—Celluloid balls, made by the older method of cementing together two hemispherical cups which had the defect of soon coming apart, to remedy which it was proposed to fit the joint with a protecting strip (Fig. 46), or to divide the ball into several sections, *e.g.* four, with overlapping edges (Fig. 47). Even these methods of joining, however, proved unsatisfactory and liable to come apart after a time, in addition to which the former is difficult to carry out, and the second both troublesome and expensive. Applied to hemispherical cups, the second method offers no advantage over the underlay strip, besides which there always remains a noticeable depression at the joints, so that none of these methods properly meets the requirements of practice.



FIGS. 46 and 47.—Ordinary Method of Joining Celluloid Balls in Two or more Parts.

The following method, however, furnishes a joint which is not only durable, but fits as true as though the ball were made in one piece. Each half of the ball is toothed at the edges, the teeth being pressed inward at right angles, and bent again at a distance corresponding to the thickness of the sheet, while the celluloid is plastic, the two halves being then pressed together so that alternate teeth in each half fit inside the other and make a very firm joint, especially when fastened with a suitable adhesive. Figs. 48 and 49 show the two halves of such a ball, before and after being assembled, whilst Figs. 50–52 represent the employed mould.

This mould consists of the mould, A, and die, B, the latter being fitted, above the hemisphere, with a ring, C, the lower end of which is recessed in the form of teeth. The thickness of the tooth-shaped projections, D, must be calculated so that their outer surface fits exactly in the upper cylindrical part, *a*, of the mould. The teeth are preferably made somewhat tapering in the width and a little wider than the gaps in the ring, C. This latter may, of course, be also made in one piece with the die.

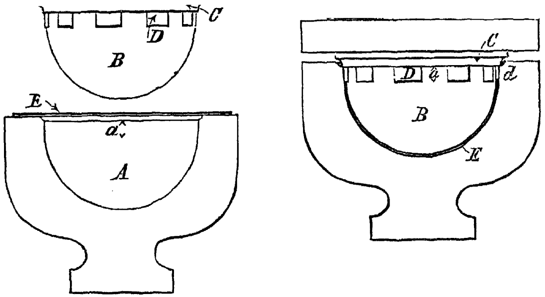


Figs. 48 and 49.—Toothed Joint for Celluloid Balls.

The celluloid sheet, E, is pressed while in a plastic state, by placing it on the mould, A, and forcing it into a hemispherical shape by the die, B. The edge of the sheet coming into position in the cylindrical part, *a*, of the mould, is cut into teeth by the teeth, D, of the die, these teeth remaining attached to the half ball and being a little narrower at the top than the gaps left between them.

The halves are taken out of the mould, the cuttings removed, and the teeth made plastic and then bent inward in the shape of a crank corresponding with the thickness of the shell of the ball. The halves are brushed over with a suitable adhesive and put together so that the teeth on each half fit in between those on the other. The adhesive is applied in such a manner that the edges also of the two halves stick together.

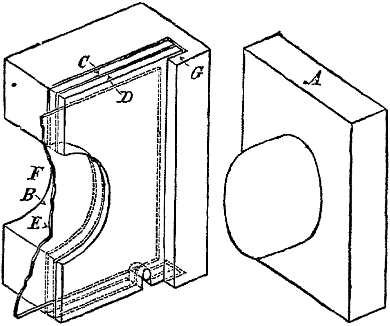
Celluloid Posters.—The celluloid posters or placards now in use consist of a sheet-metal backing over which a sheet of celluloid is stretched, and fastened at the edges by insertion into the turned-over edges of the metal. This arrangement has the defect that the celluloid, sooner or later, comes undone at the edges and springs off. In the newer makes this defect is overcome by a better method of folding the edges, namely, by doubling the metal and celluloid over twice or more.



Figs. 50, 51 and 52.—Pressing the Halves of Celluloid Balls.

Pressing Hollow Celluloid Articles.

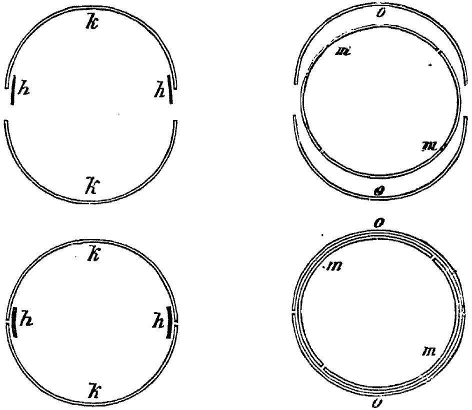
When divided metallic moulds and dies are used for pressing deep hollow bodies, these parts have to be heated, which results in the drawback that, in order to prevent loss of time in heating and cooling the presses, one attendant must have several sets of moulds and dies available. The production of these moulds and dies, however, is an expensive matter when they are all of one kind; whereas, by the newer method, one attendant with one set of moulds and dies can keep on pressing and turn out five times as many articles in the same time. Moreover, the same bottom die can be used for a number of differently shaped articles, thus reducing the cost of the die considerably. The bottom die (Fig. 53) comprises the block, B, pierced by a cylindrical opening, which may be independent of the shape of the article to be pressed, but must be large enough to take the upper die when the latter is forced down. At the top of the bottom die are two lateral guide slits, to receive the two sliding plates, C and D, and the interposed sheet of celluloid. Both these plates have circular openings corresponding with that in the bottom die, so that the celluloid sheet is left exposed in that part for the action of the upper die, whilst the edge is held between the plates. A is the top die, which, in conjunction with the lower sliding plate, determines the shape of the article to be formed.



FIGS. 53 and 54.—Dies for Pressing Hollow Celluloid Articles.

Fig. 53 represents a cross section of the bottom die with the two sliding plates, C, D, and the interposed celluloid sheet, whilst Fig. 54 shows the upper die by itself. In pressing, both the block, B, and the upper die, A, are fixed in the press, neither of them being warmed.

The celluloid to be treated is rendered plastic by heat, and is laid between the two sliding plates, C, D, with which it is slipped into the guides in the block, B, and the upper die is moved down by the press and forces the exposed portion of the celluloid sheet, E, down before it, the edges of E being meanwhile held fast by the plates, C, D. The press is now opened, the top sliding plate is drawn out, the pressed article removed, a new celluloid sheet inserted, followed by the top sliding plate, and the upper die again moved downward by the press.



FIGS. 55-58.—Device for Pressing Hollow Balls.

This rapid pressing is rendered possible by the fact that the inner sliding plates give off only just enough heat to prevent the celluloid from cooling too rapidly. At the same time, when the upper die has reached the bottom of its stroke, the celluloid has cooled sufficiently to retain its new shape. The block, B, is gradually warmed by the sliding plates, but this has no effect on the operation, since the opening in the bottom die is so wide that it does not come into contact with the pressed article.

To enable celluloid sheets of different thickness to be pressed, a spring is provided inside the guide slit or under one of the sliding plates, to hold the two plates in sufficient contact.

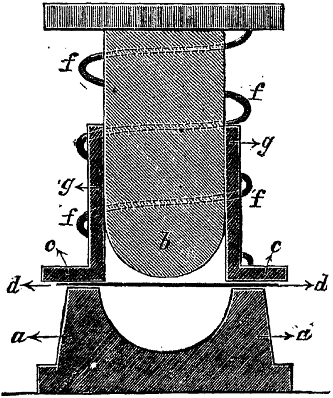


Fig. 59.—Press for Hollow Celluloid Balls.

In the method employed by the Rheinische Gummi- and Celluloid-fabrik, Mannheim, two hollow balls are made in an ordinary screw or lever press, with a divided wooden or metal mould. A section of one of these presses is illustrated, open, in Fig. 59. In this press, *a*, is the lower half of the mould, and is fixed in the base of the press, *b*, being the die or inner half of the mould, which works up and down with the movable part of the press and fits exactly in the lower part, *a*.

The construction of the three-part mould is already known; but on the other hand the arrangement of the plate, *c* (Fig. 60), is novel, this plate being pressed in any suitable way against the mould, *a*, in order to hold the inserted sheet of celluloid, *d*, uniformly at the edges. This should be one-third larger in diameter than the desired ball.

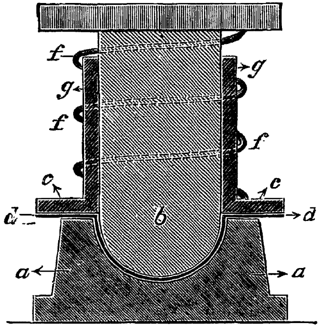


FIG. 60.—Press for Hollow Celluloid Balls.

The plate, *c*, is pressed against the mould, *a*, by the spiral spring, *f* (Figs. 59 and 60). The plate is also fitted with guides, *g*, to prevent slipping. In the absence of this plate, *c*, the circular celluloid sheet would be pressed into the mould, *a*, in innumerable wrinkles instead of forming a smooth hemisphere of uniform thickness.

Fig. 60 shows the press closed, *i. e.* at the end of the operation; *a* and *b* represent the two halves of the mould, and *d* the sheet of celluloid which has been pressed into a hemisphere between them. During the operation the plate, *c*, is held tightly against the mould, *a*, by the spiral spring, *f*, which is in a state of compression.

When the press is opened, the part *b* rises first, until the spring, *f*, is released, whereupon the plate, *c*, also rises, and enables the pressed hemisphere, *d*, to be taken out of the press.

In fitting the two halves of the ball together, it is not sufficient to merely fasten the edges by means of an adhesive, but the joint must be strengthened by a strip of celluloid inside. The width of this strip (*h*, Fig. 55) is preferably about one-tenth the diameter of the ball, the length being equal to the periphery. The strip is first fastened inside the one hemisphere, *k*, and then cemented to the other.

The two halves may also be cemented on to a smaller ball (Figs. 56 and 58). This inner ball, *m* (Fig. 56), is made of two hemispheres, on to which the outer halves are cemented, *o* (Figs. 56 and 58), care being taken that the joints of the two balls do not coincide.

Casting Celluloid Articles.—A suitable mass for casting is obtained by dissolving 1000 parts of celluloid in an equal quantity of acetone and adding 250 parts of magnesia, 50 of levigated chalk, 220 of glycerine, 100 of ether, and 150 of spirit. This mass runs easily into the moulds and sets rapidly, so that, by drying at 20° C., the article can be turned out complete in three hours.

The following are also suitable mixings:—

1. Dinitro-cellulose	100
Zinc oxide	35
Camphor	40
Castor oil	20
Alcohol	65
Ultramarine	0·9

	(1)	(2)
2. Dinitro-cellulose	55	50
Camphor	24	25
Alcohol	35	32
Castor oil	12	10

and colour to suit.

Method for Producing Designs on Plates or Sheets of Celluloid, Xylonite, etc.—The old method of producing patterns or designs on plates of celluloid, xylonite, or similar plastic, nitro-cellulose products, was by printing or pressing, with or without the assistance of warmth, or by moulding and painting. A newer method consists in stamping a design in relief on sheets of white or yellow celluloid, then applying colours or paints, and finally imparting a polish to one or both surfaces by means of suitable rollers or plates, assisted by heat and pressure, this treatment bringing the pattern up more effectively on the polished surface of the sheet.

The mordant and colour can be applied to the printed plate by dipping the latter in a dye bath, whereby the colouring matter penetrates the hollows of the pattern and forms a thicker layer there than on the rest of the surface. The sheet is then subjected to powerful pressure, assisted by heat, between plates, which may or may not be polished according to requirements. The pressure and heat smooth the engraved surface again bringing into prominence the deeper portions which before were hardly noticeable.

If one side of the sheet is to be polished, a polished plate is pressed against the portion that was not brought into contact with the dye, and this will bring the drawing up prominently on the polished surface, though it was actually impressed on the other. This polish can also be produced on the printed surface, or on both, the result in either case being to bring out the pattern better.

The impression can be imparted to the sheet by various means, such as wire, cloth, dies, rollers, etc.; and one on both sides of the sheet can be coloured, all over or in parts, by either applying the colour locally with a brush, or dipping the sheet in a dye bath.

Imitation Tortoise-shell.—Celluloid constitutes the most suitable imitation of tortoise-shell that has ever been devised; and imitations of this kind are supplied by celluloid makers, besides which they are made by consumers. The celluloid sheets employed for this purpose range from $\frac{1}{25}$ to $\frac{1}{8}$ of an inch in thickness. The ground colour of real tortoise-shell is a faint brownish yellow, to imitate which the celluloid is stained with picric acid in the process of manufacture, the solution containing also a little aniline brown, picric acid by itself being too yellow.

The reddish-brown spots so characteristic of tortoise-shell are imitated by dabbing on an alcoholic solution of aniline brown, with a little fuchsin to bring out the reddish tone. As celluloid is softened by strong alcohol, these solutions penetrate deeply into the mass. The sheets having been highly polished before applying the stain, the lustre removed by this latter operation is restored by diligent rubbing with woollen cloths. Articles of definite shape, like combs, etc., are not painted until the shaping process is completed. Incrustations of smooth-rolled metal wire, stars of thin leaf gold or silver for expensive cigar-cases and purses, small fancy boxes, etc., are pressed into the mass as already described, the latter being then smoothed, polished, and finally coloured. When the colouring is applied by a skilled operator, it is extremely difficult to distinguish the imitation from the genuine tortoise-shell by the appearance.

METALLIC INCRUSTATIONS.

Imitations of metallic incrustations, resembling metallic ornamentations inlaid in ivory (or other material), are produced on a basis of celluloid ivory by the use of real or imitation gold or silver bronze mixed to a thick fluid with collodion. The design having been painted on the celluloid sheet with this medium, the sheet is laid on a perfectly flat, thick zinc plate, and heated to 125° to 130° C., the two sheets being then passed between smooth rollers under gentle pressure. This pressure is sufficient to force the thick layer of colour or bronze into, and to unite with, the softened celluloid. Ornaments stamped out of thin sheet metal can be fixed in celluloid in exactly the same way, the surface of the celluloid being then smoothed by rubbing over gently with powdered pumice, and finally polishing with Vienna lime. If the layer of paint or bronze has been too thick, it can be reduced by rubbing down. In the case of metallic inlays, especially those made with imitation bronzes, it is highly advisable to protect the metal from atmospheric influences by a coating of transparent material, so as to preserve its pristine lustre. For this purpose, thick collodion mixed with camphor solution is poured over the celluloid, in the same way as in making a collodion plate in photography, the surplus liquid being allowed to drain off at one corner, and the celluloid sheet set up on edge to dry. After several hours have elapsed, the collodion coating is highly polished by the simple method of rubbing it with a woollen rag.

Imitation Florentine Mosaic.

Real Florentine mosaic work consists of cubes of marble or other coloured stone set together to form pictures (figures, ornaments, flowers, geometrical figures, etc.), generally inlaid in a plate of plain marble. The laborious method of production renders genuine mosaic work very expensive, which explains the desire for a good imitation. The celluloid is used in the form of sheets not more than $\frac{1}{25}$ inch thick, stained in the colours to be reproduced in the picture. The sheets should all be rolled in the same mill, so as to preserve uniformity of thickness. A large number of punches or dies of various shapes, with sharp cutting edges, are used for cutting out the tesserae.

To imitate, for instance, a mosaic picture in several colours on a black marble ground, the contours of the picture are cut with punches out of a sheet of black celluloid, which has been softened by warmth to make it plastic, and thus prevent the cracking that would occur in punching out a sheet of the ordinary hardness. For this purpose the sheet is laid on thin boards that are covered with thick sheet lead, which is warmed to about 120° C. At this temperature a sharp cutting tool will punch the plate under the pressure of the hand. The cut out pieces are laid carefully on one side, as they can be put to further use. The same cutting tools are employed to cut corresponding pieces out of other coloured and softened sheets of celluloid, a sufficient number of each being prepared to enable a large quantity of mosaic pictures to be put together at one time. This is essential owing to the high cost of the punches for each picture.

In assembling the picture the spaces cut out of the ground plate by the different punches are filled with pieces of corresponding shape and size (cut by the same punches), which fit accurately, their colour varying according to the requirements of the picture. For this work the plate must be laid on a thick and perfectly flat zinc plate, the finished picture being covered by a second zinc plate and the whole warmed to 100° C., whereupon it is passed through smooth rollers under very gentle pressure and set aside to cool. The warmth will have caused the pieces composing the picture to expand so that the edges unite, and this union is strengthened by the pressure employed, so that there are no joints visible between the pieces, and the whole picture, built up of many parts, has become as one. The picture is then rubbed quite smooth with powdered pumice, and polished with Vienna lime. If carefully made, it forms such a perfect imitation of a genuine Florentine mosaic picture that the difference can only be detected by careful examination. To fasten the mosaic sheet on a backing of slate or wood, the surfaces to be fixed together are roughened and coated with a liquid prepared by dissolving 10 parts of shellac and 5 of camphor in 40–50 of alcohol. They are then laid in contact and subjected to gentle pressure for several hours, by which time they will have firmly united.

CELLULOID COLLARS AND CUFFS.

These are made of sheet celluloid, not more than $\frac{1}{25}$ inch thick, that has been whitened with an admixture of zinc white added in the making. White lead must not be used for this purpose, as it would soon turn yellow, and finally grey, under the action of the perspiration. The moulds for these articles are made as follows. A well-starched, new, best linen collar (for example) is spread out on a zinc plate, and from it is made a plaster cast which accurately reproduces both the stitching of the seams and the texture of the fabric. A similar cast is taken of the underside of the collar, and from these casts type-metal moulds are prepared. The sheet celluloid, stamped out to the proper shape, is laid in the previously warmed mould, and on pressure being applied, the softened celluloid is forced into all the irregularities in the moulding surfaces which it reproduces. When the mould has cooled, the flat collar is taken out, bent round over a tinned iron pipe heated by steam, and passed between quick-running rollers covered with soft cloth so as to produce a high gloss.

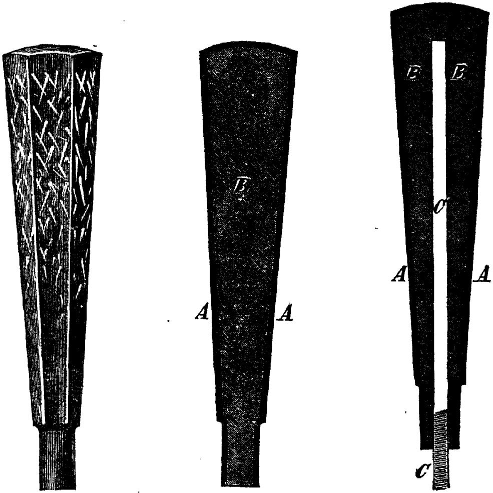
PHONOGRAPH CYLINDER COMPOSITION.

The older method of reproducing original phonograph records on to celluloid cylinders consisted in making an electro from the original record, and inserting in the electro (which carried the record on its inner surface) a celluloid cylinder, which was then warmed and suitably pressed against the electro. These records, however, are not very durable, neither are they sufficiently loud and pure in tone. An improvement is effected by replacing ordinary celluloid by a mixture of celluloid and stearic acid, the cylinders furnished by this compo. reproducing the original perfectly, and giving a stronger, more resonant and life-like tone. The stearic acid may be added to the celluloid in the process of manufacture without any other alteration in the composition of the mass.

MAKING UMBRELLA AND STICK HANDLES OF CELLULOID.

The methods of making these articles are too numerous to mention in the space at disposal, but attention may be drawn to the method of Schreiner and Siever for imitation "tiger's eye" handles.

These are made of transparent celluloid, A (Figs. 62, 63), hollow and of any shape, the interior being filled with colophony, resin, or any other fusible, brittle material, as at B, and the two ends closed with celluloid.



FIGS. 61, 62 and 63.—Stick and Umbrella Handles.

The handle is then tapped gently and shaken, so as to produce innumerable small cracks in the brittle filling. When polished, the handle has the appearance of a solid article but with a beautiful and novel appearance. The strength of these handles can be increased by a thin core of wood or iron, C, which must not fill up the whole of the interior, but leave sufficient space for the resin. The method can also be applied to making paper weights, door handles, buttons, etc.

Celluloid Dolls.

The parts of the doll are rough pressed, so that there is little strain on the materials, especially at the joints, in finishing. These parts are laid together in a properly warmed mould and pressed, the edges being coated with an adhesive if necessary. The press unites the parts and also cuts off all the surplus material (flanges). The joints and other portions of hollow parts that are most exposed to bending, pressure, and other strains when in use are strengthened by backing with small plates moulded to fit the parts and extending a short distance on either side the joints. When these backings are dry, so that they will not get out of place in the blowing process, that is to say, when the backed places are as dry as the rest, the rough-moulded hollow article is placed in the finishing mould and blown in the usual manner.

Celluloid for Ships' Bottoms.

A coating of celluloid has been successfully employed as a protection against parasitic growths, etc., on ships' bottoms. A trial sheet about nine square feet in area and $\frac{1}{16}$ inch thick, quite transparent and free from any mineral adjuncts or paint, was fixed on the bottom plates of a small screw steamer. Examination, repeated annually, showed the celluloid to remain quite free from plant or crustacean growths, whereas the rest of the bottom was so dirty as to need cleaning. After four and a half years the celluloid plate exhibited not the slightest alteration in strength, elasticity, or character. Celluloid varnish was not tried, as it necessitates a surface warmed to 36° C. before it can be applied. Owing, however, to the high price of celluloid and the difficulty of attaching it to the ship's plates, the practice will scarcely come into vogue.

CELLULOID PENS.

These are made in France by stamping out thin sheets of celluloid, ebonite, vulcanite, etc., in the form of pens, which are then perforated, and pressed in hot moulds to give them the right shape. After being cooled in water the splits are cut with a knife.

COLOURING FINISHED CELLULOID ARTICLES.

Though celluloid is obtainable in a variety of colours, it is sometimes necessary to stain finished articles another colour. As a rule, coal-tar dyes dissolved in spirit make excellent stains for this material; and for special purposes the following methods are recommended:—

Black.—The article is dipped first in weak alkali, then in dilute silver nitrate, and left to dry in the sunlight.

Blue.—A solution of indigo nearly neutralized with potash is used, or a solution of Prussian blue; or a bath of ferric chloride followed, after drying, by one of potassium ferrocyanide.

Green.—The article is dipped in a solution of 2 parts of verdigris and 1 of sal ammoniac.

Yellow.—The article is dipped successively into a solution of lead nitrate and one of yellow chromate of potash.

Brown.—A solution of potassium permanganate, made alkaline with soda, is used.

Red.—The articles are first dipped in water, slightly acidified with nitric acid, and then in an ammoniacal solution of carmine.

Purple.—Immersion in dilute chloride of gold, followed by exposure to strong sunlight.

PRINTING ON CELLULOID.

For ordinary lettering, etc., or showing up fine-coloured lines, celluloid may be printed in the usual way. The material, however, has to be specially prepared so as to obtain a matt or rough surface of suitable grain (by hand-work, sand-blast, or other means), leaving, if necessary, certain parts of the surface intact. The sheet or plate is swilled with water or alcohol, to free the depressions from any clogging, adherent particles, and is then coated with a varnish made of 2 parts of boiled linseed oil, 1 of white copal varnish, and 1 of refined ethereal oil, preferably oil of turpentine or lavender. The varnished plate is wiped to force the varnish into the artificial pores of the grain, leaving the surface bare, and is then covered for several hours with a mixture of equal parts of finely powdered magnesium and barium sulphates, after removing which it is carefully satined. This treatment gives a surface containing, enclosed in its innumerable fine pores, a very thin, almost transparent layer that exerts chemical attraction on the fatty bodies in printing ink which absorbs and retains them like paper. The most delicate drawings and shades of colour can be printed on this surface without risk of running or clogging.

According to F. Meyer (Bingen), printing on celluloid is performed as follows. On the one hand, the desired pattern, etc., is printed on paper or like substance, and on the other, the celluloid is moistened with a known solvent, such as alcohol, ether, etc. On pressing the paper and celluloid together a portion of the ink on the former is transferred, intimately coalescing with the softened surface of the celluloid, thus forming a waterproof design.

J. Artner's improvements in printing on celluloid relate more particularly to collars, cuffs, and other washable apparel, with the object of protecting the applied colours from the perspiration of the body and friction with other clothes. In contrast to existing methods of printing celluloid, the method adopted is to coat the printed surface with a transparent film, protecting the colours from contact with perspiration, other clothing, and from water in washing.

The colours or designs are applied by rollers engraved in relief so that they are printed and pressed in at the same time. The celluloid articles are then dried and coated by dipping in a warm, transparent hard-drying varnish which softens the surface of the celluloid and forms a coating that hardens on cooling, thus preventing the colours from rubbing off.

This treatment can be applied to all celluloid articles, is simple and reliable, furnishing a product capable in a high degree of resisting external influences. The varnish used is a solution of copal in ether, with alcohol and water, and a trace of oil of turpentine, the proportions being:—

Copal dried at 100° C.	6·48	per cent
Alcohol	16·40	,,
Water	1·20	,,
Ether (sp. gr. 0·725)	75·47	,,
Oil of turpentine	0·45	,,

The copal is dissolved in the ether, the solution diluted with the alcohol and water, and the oil of turpentine added last. The ether has a slight solvent action on the celluloid and assists in binding the varnish, whilst the oil of turpentine prevents the varnish cracking off.

The printed and varnished articles are finally dried at 50° to 55° C.

Neupert (Altona) prints waterproof patterns on celluloid plates by graining the latter with equal parts of wax and potash, together with water, and oil of turpentine if too thick. A pattern applied to this surface by means of an alcoholic solution of colouring matter will partly dissolve the wax (by the alcohol and alkali together) and give a sharp impression. The case is parallel to the result obtained with sized paper in comparison with unsized, the dissolved colour in the present case penetrating through the wax to the celluloid below, whereas the colour would run on the untreated celluloid.

The Rheinische Gummi- and Celluloid-fabrik replace alcohol by acetic acid for dissolving the colouring matter, and thus dispense with the preliminary treatment of the surface. Probably this is due to the fact that this solvent attacks celluloid and thus penetrates it and is at once absorbed.

The running of the colour on certain kinds of celluloid can be prevented by moistening the surface with oil of turpentine or melted paraffin wax.

Koller's Celluloid Substitute.—Highly concentrated collodion, prepared by immersing nitro-cellulose in ether-alcohol, methyl ether, acetic ether, acetone, or mixtures of these, until the solvent is completely saturated, is mixed in an autoclave with a pulpy mass of nitrated cotton or paper that has been steeped with oil of turpentine containing sulphur, castor oil and resin, turpentine resin, shellac, colophony, mastic, Canada balsam or copal resin, in solution. The mixture is carefully heated in an autoclave to 100° to 150° C., the pressure being raised simultaneously to 12 atmospheres by means of an air-pump. The resulting perfectly transparent, gelatinous mass can be converted, for example, into thin sheets serving to carry a sensitive layer of emulsion for photographic purposes, or can be cut with zigzag edges and pressed into tubes or belts.

Xylonite or Fibrolithoid.—This is a variety of celluloid in a solid or liquid form. The latter is obtained by dissolving 40 parts of nitro-cellulose in 20 parts of cedar wood oil, and 40 of amyl acetate, and is used as a dipping lacquer for metals of all kinds; the solution can also be applied to all kinds of textile fabrics. To obtain solid xylonite the solution is evaporated. Another recipe reads: Nitro-cellulose 10 parts, amyl acetate 30, amyl alcohol 25, cedar-wood oil 2, benzine 3.

Xylonite is prepared as follows, according to the patent specification: the dried finely divided pyroxylin compound is treated with a solution of camphor in a solvent that does not dissolve pyroxylin. The solvent is then expelled and the mass is finally exposed to hot alcoholic vapours.

Streubel's Vegetalin.—Dry cellulose at 15° C. is suffused with sulphuric acid (58° C.) and left in contact therewith for some little time, after which the acid is washed out completely with water, the cellulose being then dried and milled. It is next intimately mixed with resin soap in a mortar and treated with a solution of aluminium sulphate. The mixture of modified cellulose and aluminium resinate is dried, and pressed into blocks in a hydraulic press. The blocks are cut into sheets, which in turn are moulded into the desired shape by means of hydraulic pressure.

Celluloid and Cork Composition.—According to the method of Hagemann, ground cork is impregnated with a solution of nitrated cellulose in ether and alcohol, and pressed into moulds, the pressure being maintained until most of the solvent has evaporated and the mass retains its shape when the moulds are opened. For small articles this takes four to six days, and to facilitate evaporation the moulds are perforated and lined with wire gauze. The product known as "Subrit" is used as a substitute for cork, bottle corks, insulating plates, etc.

Celluloid Films for Photography and the Cinematograph.

The use of films of celluloid in place of glass plates for photographic purposes was first patented by Reichenbach in 1889; but his formula, containing hygroscopic solvents, did not yield perfectly clear films. Since that time great improvements have been made, perfectly clear, and practically colourless films of celluloid being now produced of considerable width and almost any length. The films first used were cut to the usual sizes of photographic plates and were fairly thick. These are still used in the ordinary cameras in the form of film packs which can be inserted into the camera even in ordinary daylight, and exposed one after the other until the whole pack has been used without opening the camera at all.

A further advantage was gained by having the film in the form of a roll which could be unwound as required for exposure and rewound, thus taking up but little space in the camera, an industry which has been greatly developed by the Kodak Company, and has extended the use of photography to an enormous extent. This made possible the taking of a continuous series of pictures at short intervals, and is the basis of the modern kinematograph industry which has become one of the most, if not the most, important industry in the world to-day. The films employed for this purpose are much thinner than the original and of enormous length, and contain many thousand separate pictures taken at definite but very short intervals of time, the projection of which on to a screen by means of a special kinematograph lantern, in which the pictures quickly follow each other, gives the illusion of a moving or animated picture.

These films are prepared either by passing a transparent celluloid mass through rolls until it is sufficiently reduced in thickness and extended in length, or by drawing it out in a thin plastic condition through an orifice.

In the preparation of films the Soc. Civ. des Pellicules Nouvelles pour Cinématographes et autier Usages (French Pats. 384,111, and 384,112 and additions), prepares a thick collodion by increasing the ratio of alcohol to ether usually employed by about 15 per cent. This solution is caused to flow from a receiver slowly under a pressure of 3 to 10 atmospheres issuing from a rectangular aperture which may be any size from a few centimetres to one metre in length, and up to 0·8 mm. in width.

As the product issues into the air it loses the solvent by evaporation but only slowly, thus the rate of flow must be adjusted so that the celluloid becomes sufficiently strong to bear the tension. It is drawn as a continuous ribbon or sheet by means of an endless band of cloth which carries it through a drying chamber in which it is dried by a current of heated air. The film is then denitrated by any of the usual processes, and is bleached if necessary. It is then partially dried and passed through heated calendar rolls which complete the drying and polish the films, at the same time extending their area by about 20 per cent.

A suitable composition is 100 kilos of pyroxylin in 400 litres of alcohol and ether, with sufficient camphor or other substance to render the films flexible. The sheets may also be polished by submitting them to powerful pressure in a press heated to a temperature of about 100° C.

CHAPTER VII

RENDERING CELLULOID UNINFLAMMABLE

OWING to the ease with which celluloid takes fire, and the vigour of its combustion, there is a certain amount of danger in using it where heat is present. For this reason many attempts have been made to render it uninflammable.

The methods of denitration mentioned under artificial silk (p. 95) are obvious ways of rendering nitrocellulose uninflammable, but the product formed is practically the same as the original cellulose, and will therefore burn, although not more readily than ordinary cotton or paper. The case is somewhat different with celluloid, which is a compact material more or less resistant to the action of liquids, and therefore can only be affected by adding to it during the manufacture some material which is itself non-inflammable, which evolves a gas that does not support combustion, or which on heating fuses and thus forms a protective coating to the organic material with which it is combined. The various processes which have been published may be grouped under one or other of these headings.

Most of the patents are for use of metallic chlorides, which are no doubt useful since they are soluble in alcohol and other organic solvents, and are uninflammable in themselves, but several of the chlorides evolve hydrochloric acid or chlorine on heating, and are for this reason doubly effective. The following patents relate to the use of various chlorides for rendering celluloid non-inflammable:—

W. C. Parkin (French Pat. 344,501, 1904). One part of aluminium chloride, strontium chloride, magnesium chloride, or calcium chloride (or a mixture of two or more), dissolved in two parts of methyl-alcohol, incorporated with two parts of celluloid dissolved in three parts of acetone.

A. D. Prost and E. Mickey (French Pat. 351,555, 1905). Nitro-cellulose is dissolved in acetone, ether-alcohol, or other solvent containing in solution sufficient mineral salt to render it non-inflammable. Suitable salts are alum, zinc chloride, aluminium chloride, etc. As a further protection the finished articles may be steeped in a solution of an alkaline carbonate or silicate, so as to form a surface layer of an insoluble carbonate or silicate. In an addition to this patent they quote the following proportions: Fused zinc chloride, in alcoholic solution, 10 to 25 per cent.; ammonium chloride, in alcoholic solution, 1 to 5 per cent.; carbon tetrachloride, 1 to 15 per mille.; and glycerin, 5 to 10 per cent.

In the patent of W. J. Stevens (Eng. Pat. 4390, 1908), two mixtures are given, the first consisting of nitro-cellulose 150 parts, zinc chloride 100 parts, camphor 70 parts, amyl-acetate (or acetate of other alcohol which is insoluble in water) 150 parts, sodium carbonate 15 parts. The second formula consists of nitro-cellulose 153 parts, methylated spirit 100 parts, zinc chloride 100 parts, amyl-acetate 200 parts, and sodium carbonate 15 parts.

P. A. D. Prost au Les Fils Pinay-jeune (French Pat. 421,854, 1911). In this patent the method of making nitro-cellulose is described. The latter is placed in a receptacle and moistened with a solution composed of ether-alcohol 1000 c.c., stannous chloride 300 to 400 grams, camphor 300 to 400 grams, ammonium or barium chloride 3 to 10 grams, sodium chloride 1 to 5 grams carbon tetrachloride 20 to 40 grams, lactic acid 15 to 50 c.cm., and castor oil 10 grams.

J. Nigro and P. C. A. Hollande (French Pat. 420,212, 1910). A solution of 1 part of celluloid, or like material, in 10 parts of acetone mixed with one part of magnesium chloride dissolved in three parts of alcohol.

Stocker's Uninflammable Celluloid is made as follows: 100 parts of nitrated cotton or paper are mixed with 400 parts of camphor and 70 parts of stannous chloride, the whole being moistened with 100 parts of alcohol. After standing twelve hours the mass is heated to 70° C. by passing it through warm rollers, and is kneaded until it becomes perfectly homogeneous. By increasing the proportion of alcohol, the mass can be kneaded and worked in the cold.

This process furnishes a transparent mass, which can be worked in the usual way. To obtain coloured products, cupric chloride is added for green, or ferrous chloride for brown or black, or aniline dyes may be used. The mass will burn only when held directly over a flame, and ceases to burn or even glow immediately it is removed. For special articles, such as cartridges, that are desired to be combustible, the proportion of stannous chloride may be reduced.

An alcoholic solution of calcium chloride, of about 20 per cent. strength, is added to an acetone solution of celluloid, about 10 per cent. strength, in such proportion that one part of calcium chloride is present to 10 parts of celluloid. The solvent is evaporated and the celluloid is rolled into thin sheets which are dried at the ordinary temperature. The proportion of calcium chloride may be increased to 15 or 20 per cent. The calcium chloride may also be added to the celluloid, which is then moistened with alcohol and milled at 20° C.

Magnesium chloride may also be employed in the proportion of six parts of the salt dissolved in alcohol to 25 parts of celluloid solution. Asbestos may also be worked in with the pulp.

By the use of aluminium chloride or nitrate in a saturated solution in acetyl-acetate the material is rendered non-combustible, and it is stated that the camphor may be partly or entirely dispensed with.

Other methods of rendering celluloid uninflammable are as follows:—

The addition of bromates and ferrous chloride to the celluloid solvent results in the liberation of gases when the celluloid is heated and thus stifles combustion.

A non-inflammable celluloid can be produced by incorporating with the paste made from nitro-cellulose and acetone a salt which on heating will liberate a large volume of a gas which will not support combustion, as, for instance, a bicarbonate (P. Germain, French Pat. 349,292, 1904).

The celluloid in its plastic condition (90 parts) is mixed with a siliceous ether (10 parts), such as amyl or methyl silicates, *i. e.* tetra-ethyl monosilicate, diethyl-monosilicate, hexa-ethyl disilicate, or diethyl-disilicate, which are formed by the partial hydrolysis of a normal silicic ester (E. F. Clement, French Pat. 402,569, 1909).

The pyroxylin or other cellulose ester (*i. e.* acetate, etc.), is mixed with chlorinated stearic acid or other halogen-substituted fatty acid (J. W. Aylsworth, U.S. Pat. 961,360, 1910).

The use of acetyl-cellulose is also claimed for rendering celluloid uninflammable. In the patent of W. C. Parkin and A. Williams (Eng. Pat. 26,657, 1909), a method is described for producing a mixed nitrate and acetate of cellulose, by employing acetic anhydride with nitric and sulphuric acids.

The addition of metallic resinolates to celluloid or collodion renders the finished product uninflammable (French Pat. 439,648, 1911). The patent apparently relates to the preparation of an insoluble metallic soap and not to a resinate.

Nitro-cellulose 1 kilo, fish glue 1·5 kilos, gum arabic 400 grams, gelatin 100 grams, and castor oil 40 grams: the incorporation of these materials with the nitro-cellulose is said to render it non-inflammable (French Pat. 344,048, 1904).

Boric acid, either in the form of an alcoholic solution or as a dry powder, is incorporated with the celluloid mass (French Pat. 347,446, 1904).

One part of nitro-cellulose, one part of camphor, and two-and-a-half parts of amyl-acetate are mixed with four parts of a super-saturated solution of magnesium sulphate. A number of other salts easily soluble in water and capable of resisting heat are mentioned (H. Lagneau, F. J. Nebel, and M. E. Vines, French Pat. 360,912, 1905).

The bleached nitro-cellulose, containing 40 to 50 per cent. of water, is combined with five per cent. of a liquid hydrocarbon, essential oil of aspic by preference, and colouring matters if required. The product is submitted to the action of a mixture of alcohol, ether, acetone, and amyl-acetate for a period of about six hours. The plastic mass thus formed is rolled out into dough between rollers heated to 60° C. and is sprinkled with a mixture of ether, boric acid, calcium ethylate (75 per cent.) and ammonium sulphocyanide, which are incorporated with the sheet by further rolling. The product is transferred to a strong receptacle in which it is submitted to a pressure of 150 atmospheres, and it is kept under pressure while it is undergoing cooling by a current of cold water (L. Bèthisy, L. Fouchard, and E. Vignes, French Pat. 368,004, 1906).

To a solution of celluloid in acetone or methyl-alcohol is added an acetic-acid solution of a metallic salt, which is insoluble in water and alcohol. The proportion of the salt used is 3 parts to 15 parts of celluloid. A large number of suitable salts are mentioned, including ferric phosphate, barium phosphate, and lead nitrate. To this material, carbon tetrachloride, trichlornitro-methane, and a nitro-hydrocarbon are added, and the mixture is kept in a closed receptacle till the solvents have penetrated the mass. Solution of formaldehyde is next added and allowed to act for ten hours, when the celluloid separates from a liquid portion. It is then removed and after partial drying is worked up in the usual manner.

CHAPTER VIII

EMPLOYMENT OF PYROXYLIN, OR NITRO-CELLULOSE, IN THE PREPARATION OF LACQUER VARNISHES

Solubility of Nitro-cellulose.—As prevously remarked, the solubility of nitro-cellulose, generally speaking, depends upon the amount of nitrogen present in the nitro-cellulose, or upon the extent to which nitration has been carried, the hexanitrate being insoluble in ether-alcohol while the tetranitrate is entirely soluble. By varying the method of treatment, however, nitro-celluloses containing a high percentage of nitrogen can be obtained which are quite soluble in ether-alcohol.

In this connection MacNab * says:—

"The composition of the acid mixture is of the greatest importance and largely determines the character of the product. The ratio between the nitric acid, sulphuric acid, and water must be accurately adjusted.

"With the same ratio of sulphuric acid to nitric acid the amount of nitrogen in the nitro-cellulose decreases as the water is increased in the mixed acids.

"Alterations in the ratio of the acids has not much effect with the lower percentages of water, but increase of the sulphuric acid leads to increase of nitrogen when the water is about 14 per cent. or over. It thus becomes possible to produce nitro-celluloses with the same amount of nitrogen with acid mixtures containing different quantities of water. The solubility in ether-alcohol also increases as the water is increased in a nitrating mixture of the same ratio of acid, while with the same amount of water the solubility decreases as the sulphuric acid increases.

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* Inst. of Chem. Lectures on Explosives, p. 45.

"The products of nitration are not formed in clear-cut stages of mono-, di-, tri-, etc., nitrate, rather it may be said that, within limits, any percentage of nitrogen can be produced by selecting a nitrating bath of suitable composition.

"The composition of the nitrating bath in the 'displacement' process may be taken as: sulphuric acid 71, nitric acid 21, water 8. This yields a gun-cotton containing about 13 per cent. of nitrogen and nearly insoluble in ether-alcohol, whereas a bath containing sulphuric acid 56·7, nitric acid 28·3, and water 15, would give a nitro-cellulose containing about 12 per cent. of nitrogen, and entirely soluble in ether-alcohol. The explosiveness of the nitro-cellulose increases with the nitrogen in it.

"It must also be remembered that the cotton is by no means a definite chemical body, and its physical state plays an important part. Samples of different cottons, under the same conditions in a bath of the same composition, while yielding nitro-celluloses containing practically the same percentage of nitrogen, may vary in solubility in ether-alcohol from 25 per cent. to 70 per cent. In some cases the viscosity of the ether-alcohol solution is of importance; this again is affected by the nature of the cotton and, with the same nitrating bath, different cottons may show great differences in viscosity."

Walter D. Field also compares the solubility of two products made with different strengths of acid. In the one case the cotton is immersed for ten to twelve minutes at 60° C. in a mixed acid consisting of nitric acid (sp. gr. 1·435), 33, sulphuric acid (sp. gr. 1·83), 65·5, and water, 1·5. This yields a nitro-cellulose which is very friable, and is readily soluble in methyl-alcohol and all hygroscopic solvents yielding solutions which are very fluid. In another case the cotton was immersed at 65° C. in a mixture containing the same proportions of the two acids, but rather more water, its percentage composition being nitric acid (sp. gr. 1·435), 32·6, sulphuric acid (sp. gr. 1·83), 65·1, water, 2·3. The product formed in this case was still more easily soluble in methyl-alcohol than the preceding one. If, however, a weaker nitric acid be used (*i. e.* sp. gr. 1·40), and no water be added, the proportions being approximately the same as in the last example, the product is quite different, whereas the former is imperfectly soluble in non-hygroscopic solvents, the latter is freely soluble, while its solutions in the hygroscopic solvents are inclined to be heavy. Another property which is observed in the product made with the mechanically added water is that on drying to a film it yields a much more contractile film on evaporation than do other nitro-celluloses.

A. Mattesschat * has compared the solubilities of a nitro-cellulose containing 12·95 per cent. of nitrogen in mixtures of ether (sp. gr. 0·720) and alcohol of various strengths, and obtained the following results:—

	Solubilities.			
	Alcohol 99·5 per cent.	Alcohol 95 per cent.	Alcohol 90 per cent.	Alcohol 80 per cent.
	per cent.	per cent.	per cent.	per cent.
Alcohol : ether 1:1	52·3	42·3	28·7	14·2
Alcohol : ether 2:1	40·5	52·4	53·9	45·0
Alcohol : ether 3:1	25·0	42·4	53·0	57·5

With regard to the effect of heat upon the solubility of nitro-cellulose, E. Bergmann † has shown that it is materially increased. Thus a nitro-cellulose which had an initial solubility of 4·7 per cent. in ether-alcohol, after heating at 132° C. for six hours, had its solubility increased to 82·5 per cent.

The solutions of pyroxylin in hygroscopic solvents, such as ether-alcohol, acetone, etc., yield on evaporation films which are cloudy or opaque, the appearance thus presented being ascribed to the absorption of water during evaporation, and the consequent partial precipitation of the nitro-cellulose in an amorphous insoluble form. On the other hand solutions in non-hygroscopic solvents, such as amyl-acetate, yield clear films, the nitro-cellulose in this case remaining homogeneous and in a truly colloidal form.

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* *Z. ges. Schiess und Sprengstoffw*, 1914, 105. *Journ. Soc. Chem. Indt.*, 1914, 376.

† *Z. Angew. Chem.*, 1904, pp. 982, 1018, 1074

The property of forming clear films from pyroxylin was first utilized by Richard Hale (U.S. Pat., No. 471,422) for the manufacture of varnishes for brass and silver ware. Hale used as a solvent a mixture of 4 parts by volume of amyl-acetate, 4 parts of petroleum naphtha, and 2 parts of methyl-alcohol; adding pyroxylin in the proportion of 4 to 5 oz. per gallon of solvent.

The manufacture of varnishes or lacquers from nitro-cellulose has been greatly extended, and now includes the preparation of bronze and aluminium paints and the manifold aeroplane "dopes," which were in great demand during the late war. Most of the latter are prepared from nitro-cellulose with one solvent or more, their chief characteristics being the small amount of solid matter present, yielding very thin and light, but perfectly continuous films, and their great contractability which induces that shrinkage of the fabric which yields a drum-like tightness. Neither of these properties are to be found in the ordinary paints and varnishes.

C. M. Jacob (Eng. Pat. 3605, Sept. 14, 1876) uses a solution of pyroxylin or gun-cotton and gutta-percha in alcohol and ethyl-ether, for sealing the stoppers of glass bottles, the necks of the bottles being dipped in the composition and allowed to dry. A thin film of the material thus covers the stopper and the neck of the bottle forming an air-tight joint.

The solubility of celluloid and pyroxylin in volatile liquids, such as ether, alcohol, acetone, etc., was utilized some twenty-five years ago for the purpose of coating metals and other substances with an extremely thin, glossy, and flexible layer of celluloid (pyroxylin). These solutions are now sold under various names, such as crystalline, Zapon lacquer, Victoria lacquer, etc., and differ from all other lacquers in that, whilst they do not impart a gloss when applied to paper, wood, fabrics, etc., and also destroy the lustre of other lacquers, they do not affect that of polished metal, glass, etc. This characteristic difference is also responsible for their extensive use, the main principle of which is to furnish a lacquer that is barely visible on the object to which it is applied, and does not affect the surface, whether this is smooth and glossy or dull, porous, etc., of the material in any way. Now, all resin lacquers, whether oily or alcoholic, are very apparent after application—the lacquer on polished metal being iridescent by reflected light, owing to the heterogeneous condition of the dissolved resin. On the other hand, the layers of celluloid lacquer are so extremely thin that they are invisible, and, if properly applied, they never cause iridescence on metallic surfaces. They adhere very tenaciously to all materials, and cannot be removed from metal by scraping, though the lacquers themselves are soft and elastic.

All other known lacquers, even those classed as "matt," produce a more or less glossy surface on matt substances like paper, wood, etc. Absorbent substances are rendered stiff and hard by taking up large quantities of the solution. Celluloid lacquers on the contrary do not interfere with the gloss of metal or glass, they leave the properties of paper, wood, etc., unchanged, whilst absorbent substances are left soft and flexible, owing to the peculiar properties of celluloid. The differences between the ordinary resin lacquers and celluloid varnishes are due to the fact that the former contain much more solid matter in solution: for instance, shellac lacquers will contain at least 7 per cent. of the resin, whereas celluloid varnish may contain not more than 1 per cent. of nitro-cellulose. It is clear that such a lacquer is suitable for very extensive use, and in fact it can be applied to all manner of objects: to metals (to prevent tarnishing), to cementing celluloid articles, as a fixing varnish for drawings, document varnish, printing lacquer for painting on fabrics, map varnish, playing-card varnish, dolls' heads, toys, staining and matting glass, etc. Moreover, it is easy to use, no skill in manipulating a brush being required; and there are no troublesome bubbles, raised edges and drops as with spirit varnishes. The celluloid varnish is either poured upon the article or used as a dipping bath, though celluloid varnishes containing slow-drying solvents have been introduced for brush work, and a combination of various volatile solvents has also enabled matt celluloid varnishes to be prepared. The coatings dry very quickly, and will last for years without cracking or peeling.

Celluloid varnishes are prepared from dry or spongy celluloid, or from nitro-cellulose and camphor. They should be made in closed vessels, fitted with stirrers, which are heated gently by steam or hot water. The resulting solutions should be quite clear, or they should soon clarify on standing, filtration being difficult owing to the volatility of the solvent and inflammable nature of the material, and the ease with which the filtering material becomes choked and ceases to act.

Acetone, sulphuric ether, alcohol, amyl-acetate, amyl-alcohol and various acetic esters, chlorhydrins, etc., can be used, together or separately, as solvents. A suitable mixture consists of acetic acid and amyl-acetate; another of amyl-alcohol and alcohol; a third of amyl-acetate and alcohol; a fourth of acetic ether, acetic acid and ethyl-ether; and a fifth of amyl-acetate and amyl-alcohol. Transparent celluloid, swollen by steeping in amyl-acetate, will dissolve in equal parts of alcohol and oil of turpentine, and also in amyl-acetate, to a clear solution, but gives a matt coating on metal. To dissolve celluloid it is cut into small pieces, left moistened with alcohol or ether for some hours, and then placed in the solvent. The following proportions will give good results:—

1.	Celluloid	5 parts
	Amyl-acetate	16 ,,
	Acetone	16 ,,
	Ether .	16 ,,

2.	Celluloid .	10	parts
	Ether . .	30	
	Acetone .	30	
	Amyl-acetate	30	
	Camphor .	4	
3.	Celluloid .	5	
	Alcohol .	50	
	Camphor .	5	
4.	Celluloid .	5	
	Amyl-acetate	50	
5.	Celluloid .	5	
	Amyl-acetate	25	
	Acetone .	25	

Collodion is the oldest and best-known varnish made from pyroxylin. It is officinal in the British Pharmacopœia, and is made by dissolving 1 part of pyroxylin in 12 parts of alcohol (90 per cent. strength) and 36 parts of ether (sp. gr. 0·735). Collodion is extensively employed for surgical purposes, principally for applying to wounds, which it covers with an impermeable coating, thus keeping out air and infectious organisms; it is also used for sealing bottle-stoppers and in the preparation of photographic plates and papers, for which purpose it was first employed by Scott Archer in 1884.

Hall prepares varnish from nitro-cellulose by dissolving 2½ lb. of pyroxylin in 4 gallons of amyl-acetate and 4 gallons of coal-tar benzol. Wilson dissolves nitro-cellulose in amyl-acetate, and another recipe gives 1 part of collodion wool to 6–7 of dinitro-toluol. Tscheuschner dissolves nitrated vegetable fibres in ether-alcohol containing boric acid; and zinc chloride dissolved in hydrochloric acid is also said to be a solvent for celluloid.

The following proportions will yield good varnishes:—

1.	Nitro-cellulose . .	100	parts.
	Amyl-acetate . . .	150	
	Amyl-alcohol . . .	400	
2.	Methy-alcohol . . .	32	
	Amyl-butyl or propyl-acetate	18	
	Amyl-alcohol . . .	32	
	Soluble pyroxylin . .	5	

3.	Methyl-alcohol	44 parts
	Amyl-alcohol	10 ,,
	Propyl or butyl alcohol	20 ,,
	Camphor	5 ,,
	Soluble pyroxylin	10 ,,

BOLTON'S RECIPE.

Nitro-cellulose from paper	30 parts.
Camphor.	10 ,,
Alcohol	1000 ,,

When collodion cotton is used, 10 parts of the dry cotton are moistened with 35 of ether, followed by 60 of 95 per cent. alcohol. The solution is allowed to stand and the clear liquid decanted, and four to six parts of camphor are stirred into the clear solution.

The difficulty of dissolving celluloid in alcohol has been overcome by The Cie. générale Chromolithographie de Paris, by converting the celluloid into a spongy mass by the aid of a vacuum, or else by disintegrating the cellulose mechanically and then drying it quickly. In this way the solvent power of the alcohol is increased four to five fold, and at the same time the treatment enables other ingredients to be introduced which facilitates the application of the varnish to cold and damp articles. Instead of the usual practice of drying the rolled celluloid slowly, the moist mass is placed in an airtight vessel, from which the air is then exhausted by means of an air-pump, with the result that the contained alcohol and excess of camphor evaporate rapidly, and leave the mass in a spongy condition. It is then dried quickly, to prevent the collapse of the mass to a solid condition. To make this spongy product into varnish, the following ingredients are employed: Spongy celluloid 100 parts, pure acetic ether 200, sulphuric ether 25, castor oil 5 to 10, oil of turpentine 15 to 25, denatured spirit 75, amyl-acetate 1, glacial acetic acid 20 parts. The acetic ether and acetic acid are mixed together, and after a time the celluloid is added, the mixture being agitated for 6 hours, with intervals of rest for 15 minutes every hour. After a further 6 hours the sulphuric ether is added, followed by the castor oil (dissolved in a portion of the alcohol), the whole being shaken up until completely mixed. The oil of turpentine, amyl-acetate and remainder of the alcohol are incorporated successively in the same manner, the order named being essential to success. The acetic acid and amyl-alcohol improve the adhesion of the varnish on undried articles, and in addition the varnish is far richer in celluloid than those prepared in the ordinary way, as well as opposing greater resistance to acids and atmospheric influences. The articles to be coated must be gently warmed, or the varnish will not look well, but it may be fitted for application in the cold by increasing the proportion of acetic acid by 40 parts and the amyl-acetate by 30 parts.—*Farben Zeitung.*

A new impermeable coloured varnish, for use on paper, cardboard, cloth, etc., is prepared by S. de la Grange as follows :—

1. Ten grammes of octo-nitro-cellulose are dissolved in a mixture of 50 c.c. of amyl-acetate and an equal amount of 95 per cent. alcohol, and the solution is filtered through cotton-wool.

2. Forty c.c. of castor oil, palm oil, or any other vegetable oil, are mixed with a sufficient quantity of some colouring matter, such as ochre, chrome, aniline, etc., to furnish the desired shade of colour.

These two products are then incorporated by stirring together for four hours, and applied to the paper, etc., in a machine similar to those used by the manufacturers of oilcloth, paper being preferably treated in an uncalendered condition. After a sojourn of about two hours in a drying machine, the paper is wound on a roller, and put through the calender, to supple the varnish, or else is impressed with a pattern in a stamping machine.

The same preparation may also be employed as a paint by mixing equal quantities (25 c.c.) of the two varnishes, adding thereto 50 c.c. of No. 1, and to the whole one part of amyl acetate and one part of 95 per cent. alcohol. The paint is said to adhere well to glass, iron, wood, plaster, cement, etc., and to have a brilliant gloss.

ECKSTEIN'S RECIPE.

Collodion cotton	8-10 parts.
Ether or alcohol	100 ,,
Castor oil	2-4 ,,
Resin	4-10 ,,

Celluloid bottle varnish is made by dissolving—

Pyroxylin	3-4 parts.
Boric acid	1 part.
Resin	25 parts.
Pigment	50 ,,
Ether-alcohol	100 ,,

Gérard's patent prescribes dissolving 1 part of gelatine and 2 of trinitro-cellulose in 3 of glacial acetic acid, 19 parts of acetic acid, a little glutin, castor oil and gum-lac being added. American patent 371,021 gives a mixture of amyl-chloride, acetate and chloracetate as solvent for pyroxylin; No. 372,100 mentions amyl-chloride and camphor. A. M. Dougal's English patent states that a good celluloid varnish for leaden water-pipes is obtained by dissolving nitro-cellulose in alcohol and ether and adding castor oil or Canada balsam to the solution. A little magnesia or strontia can be added to increase the strength. Camphor phenols are also said to furnish good celluloid varnishes.

A varnish for fishing lines may be made as follows:—

Pyroxylin 100 parts, castor oil 250 parts, amyl-acetate 450 parts, magnesium carbonate 2 parts, wood spirit 600 parts, all by weight (J. E. H. Hyde, U.S. Pat., 673,955, May 14, 1901).

According to the nature of the solvents used, the solutions can be readily stained with coal-tar dyes dissolved in spirit or oil, and very pretty effects can be obtained in this way. Though it would be desirable to replace these volatile and inflammable solvents by safer ones, there does not seem much likelihood of this being done.

In order to prepare a perfectly clear varnish from nitro-cellulose, the solutions have to be filtered. Owing to the viscosity of the solutions, filtration under ordinary conditions is very slow, but by applying pressure the operation is very considerably hastened. Fig. 64 shows a hydraulic

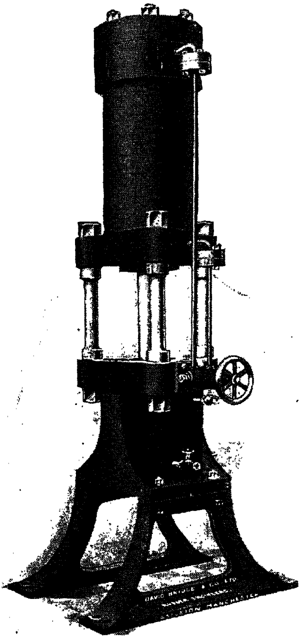

Fig. 64.—Hydraulic Solution Strainer. David Bridge & Co., Ltd.

solution strainer made by David Bridge & Co., Ltd., Castleton, Manchester, which is suitable for this purpose.

CHAPTER IX

EXAMINATION OF CELLULOID

THE qualitative examination of celluloid, that is to say, the detection of the materials present is not a difficult matter, but the quantitative estimation of the various ingredients is not so simple, and requires a considerable amount of care.

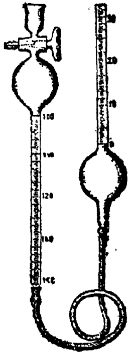

FIG. 65.—Nitrometer. Gallenkamp & Co.

The most important constituent of celluloid is, of course, the nitro-cellulose, which may be estimated directly by means of the nitrometer. Fig. 65 shows a nitrometer suitable for the purpose, manufactured by Gallenkamp and Co.

In the case of celluloid, the material must be cut up fine, a weighed quantity being placed in the bulb, where it is treated with concentrated sulphuric acid, the nitric oxide evolved being measured after allowing ample time for the completion of the reaction and the cooling down of the apparatus. The nitric oxide is reduced to normal temperature and pressure and its weight calculated, from which may be deduced the amount of nitro-cellulose, assuming it to be the di-nitrate $C_6H_8O_3(NO_3)_2$.

In that case 1 c.c. NO : ·005645 gram nitrate.
1 gram NO : 4·2 ,, ,,

This method, although sufficiently accurate in most cases, is liable to considerable errors if the celluloid contains substances as, for instance, carbonates or chlorides, which also yield gases under the same conditions. Should this be the case, an analysis of the gas would be necessary to determine the amount of nitric oxide present, but with chlorides secondary reactions would take place, resulting in the formation of nitrogen and chlorine, which would complicate matters and render the analysis of no value.

The amount of nitrogen in nitro-cellulose itself can be determined by the Schloesing method in which the material is boiled with ferrous chloride and hydrochloric acid, the nitrogen in this case being also evolved as nitric oxide. The process is, however, not very suitable for celluloid, which, being so compact, is not readily acted upon by the reagents.

The reduction brought about by these reagents results in the regeneration of the cellulose (probably as hydrate).

According to Hadow, a similar reduction can be effected in the case of gun-cotton by boiling with an alcoholic solution of sodium sulphydrate, the precipitate formed, after washing several times with alcohol and drying at 100° C., being weighed as cellulose, from which the amount of nitro-cellulose can be deduced.

H. Dubovitz* has devised the following scheme of analysis, which is simple, and easily carried out.

Estimation of Nitro-cellulose.—A weighed portion, approximately 2 grams of the finely divided celluloid is introduced into a 150 c.c. graduated flask, 100 c.c. of acetone is added, and the flask closed and well shaken from time to time until the solution of the celluloid is complete, any mineral matter which it may contain being left in a finely divided condition. The liquid is then made up to 150 c.c. with acetone and well shaken. Fifty c.c. of the liquid containing the suspended matter are quickly removed for the estimation of the nitro-cellulose and mineral matter, which are precipitated together by the addition of 25 c.c. of an 8 per cent. solution of ammonium chloride. As heat is evolved during the mixture of the two liquids, the flask must be cooled in a stream of cold water. The precipitate is collected in a Gooch crucible, washed with a mixture of acetone and 8 per cent. ammonium chloride to free it from camphor and then with alcohol, after which it is dried till the weight is constant. This represents the nitro-cellulose and mineral matter, the difference between this weight and the original being the camphor. If camphor substitutes or mineral salts soluble in acetone were present this figure would need revision.

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* *Chem. Zeit.*, 1906, p. 936.

Estimation of Mineral Matter.—To the residue in the Gooch crucible a small piece of paraffin wax is added and melted by a gentle heat. The crucible is then gradually heated to bright redness until all the organic matter has burnt away and the residue been converted to an ash. The difference between this weight and the previous one being taken as nitro-cellulose. Starch or other organic filling material would be included in this weight, but they could be separately estimated and allowed for.

Soluble Nitro-cellulose.—To the remaining 100 c.c. of the original solution 8 per cent. ammonium-chloride solution is added until no further precipitate occurs, the liquid is drained off and the precipitate pressed, removed to a 150 c.c. graduated, stoppered cylinder, in which it is shaken with 50 c.c. of alcohol for about half an hour, 100 c.c. of ether are then added, and the contents vigorously agitated from time to time until the nitro-cellulose is dissolved and the liquid is quite clear; 50 c.c. of the solution are then evaporated at a gentle heat, and the residue dried at 50° C. and weighed.

Estimation of Camphor.—A. Herve * proposed to extract the finely divided celluloid in a Soxhlett tube with chloroform, afterwards weighing the dried residue and taking the camphor by difference; but there is an objection to this method of procedure since the residue persistently retains chloroform which, according to the author, can be estimated by saponifying the residue with caustic potash and determining the chloride formed. Obviously large errors would be introduced if chlorides were present in the celluloid.

Herve suggests as an alternative method that the celluloid be distilled with water and caustic potash, when the camphor volatilizes and will be found adhering to the flask or floating on the surface of the distillate. The condenser is washed out with benzene, which is run into the distillate, with which it is shaken, thus dissolving the camphor. The benzene solution is separated, dried with anhydrous copper sulphate, and made up to a definite volume by addition of more benzene, the amount of camphor in the solution being determined by the cryoscopic method. The results are compared with a table calculated from experiments with known quantities of camphor from which the amount of camphor in the sample is arrived at.

For the estimation of camphor directly F. Foerster † recommends the following method :—A quantity of the finely divided celluloid corresponding approximately to 2 or 3 grams of camphor is weighed into a flask provided with a tap funnel and attached to a condenser. The receiver (Fig. 66), consists of a tube as shown in the figure, consisting of two bulbs, with a connecting tube which is graduated. The lower bulb has a capacity of 150 c.c. and the tube holds 30 c.c. Caustic soda of 10 per cent. strength is run into the flask through the funnel in sufficient quantity to more than saponify the nitrocellulose. The flask is heated on the water bath to 80° C., and as soon as saponification is assumed to be complete more caustic soda is run in to make the total up to 100 c.c. Water is then added up to 250 c.c. and the liquor is boiled vigorously. When the lower bulb of the receiver is nearly full the distillation is stopped and the liquid made up to the lower mark with water. During the experiment the U-tube attached to the receiver is half-filled with benzene to prevent any camphor escaping. This is added to the contents of the bulb, the condenser is washed out with a little benzene, which is also run into the bulb, the total volume of benzene being made up to 30 c.c. The contents of the receiver are shaken in order to bring the whole of the camphor into solution. The benzene can then be pipetted out, and after cooling to 20° C. it is examined in the polarimeter.

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* *Caoutchou et Gutta-percha*, 1918, p. 9601.

† *Ber.*, 23, 2, 981.

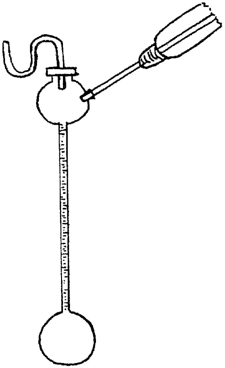

FIG. 66.—Foerster's Tube for Estimating Camphor.

The author used a Laurent's half-shadow apparatus with a water-jacketed tube 400 mm. long, the temperature being kept at 20° C. and all calculations made to that temperature.

Using camphor recrystallized from alcohol (m. p. 176·3° — 176·5° C.) he found the specific rotation to be

$$[\alpha]_D = (39{\cdot}755 + 0{\cdot}17254c)^\circ.$$

Since $$c = \frac{100\alpha}{l[\alpha]_D}$$

then $$c = 115{\cdot}2052 \left(-1 + \sqrt{1 + 0{\cdot}0436683\frac{\alpha}{e}}\right).$$

Several determinations of camphor by this method, using 5 to 40 grams, gave excellent results, the error never exceeding ·08 per cent., and in one case falling as low as ·002 per cent. A sample of celluloid examined by this process gave in two experiments 22·43 and 22·53 per cent. of camphor respectively.

E. Barthélemy * gives two methods of extraction of camphor, one of which differs only in minor details from that of Foerster, steam, preferably from a superheater, being used in the distillation, and the distillate being acidified before extracting with benzene.

If $[\alpha]_D$ is the rotation of the liquid then the formula for calculating the amount of camphor per 100 c.c. of benzene is

$$c = 2{\cdot}51536\frac{\alpha}{e} - 0{\cdot}02746\left(\frac{\alpha}{e}\right)^2.$$

A very fair approximation to the amount of camphor present may also be obtained by placing 10 c.c. of the benzene solution in a vacuum desiccator, and weighing at intervals until the weight is practically constant.

The second method is to extract 20 grams of the finely ground celluloid for 8 to 10 hours in a Soxhlett tube with light petroleum spirit boiling at 45°–55° C. and evaporating off the ether in a vacuum.

Utz † also recommends extraction with light petroleum spirit (B. P. 30°–40° C.), the solvent being evaporated in a current of cold air, and the camphor dissolved in pure methyl-alcohol. The solution is made up to 100 c.c. at

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* *Caoutchouc et Gutta-percha*, 1912, p. 6735.

† *Gumi Zeit.*, 1907, 53.

17·5° C. and is examined at that temperature with an immersion refractometer. A table showing the refractive indices of various strengths of camphor solutions has been prepared by the author, who states that the refractometer method is better than the polarimetric, since it includes both natural and artificial camphors, which have equal refractive indices, whereas the latter, being inactive, are not estimated by the polarimeter.

H. Bockmann gives the following analyses of celluloid:—

	English.	German.
Nitro-cellulose	73·70	64·89
Camphor	22·79	32·86
Colouring matter	3·51	2·25
	100·00	100·00

Stability of Nitro-cellulose.—The stability tests used in testing gun-cotton may also be applied to collodion cotton and celluloid.

The official test is to heat the material in a test-tube suspended in an oil bath, slowly, and note the temperature at which potassium iodide and starch paper suspended in the mouth of the tube becomes blued. This indicates incipient decomposition with evolution of NO. The heating may then be carried further till the material inflames, the temperature being again noted. The following results by Dubovitz show the relative stability of several samples of celluloid:—

Total Nitro-cellulose.	Camphor.	Mineral Matter.	Soluble Nitro-cellulose.	N as NO_3.	NO_3 in Nitro-cellulose.	Inflammation Temperature.
68·1	21·98	9·86	63·77	24·0	35·26	136°
64·9	35·0	0	59·1	23·96	36·78	103°
66·7	19·6	13·63	—	—	—	161°
71·3	18·3	10·43	—	—	—	131°
67·7	32·2	0	—	—	—	115°

The apparatus described by E. Bergmann and A. Junk,* which has been in use at the Prussian testing station for a good many years, consists of a copper bath with a closed top in which are fitted ten countersunk copper tubes, 20 c.m. in length. The bath is partly filled with amyl-alcohol and is fitted with a condenser so that the temperature may be kept constant at 132° C. The glass tubes used are 35 c.m. long and 2 c.m. diameter, and into the mouth of each tube is fitted, by grinding, a small set of absorption bulbs. Two grams of the material to be tested is placed in one of the tubes and pressed down, the bulbs are about half filled with water and attached, and the glass tube is placed in one of the copper tubes in the bath, in which it is heated for two hours. The oxides of nitrogen are absorbed by the water in the bulbs, which is immediately drawn over when the tube is removed from the bath. The liquid in the tube and bulbs is filtered, oxidized with permanganate, and the nitrogen estimated by the Schultz-Tiemann process.

The stability of the nitro-cellulose is measured by the amount of NO evolved, the authors stating that a stable gun-cotton evolves not more than 2·5 c.c. NO per gram when heated for two hours at 132° C., while a stable collodion cotton will yield less than 2·0 c.c. under the same conditions.

The following results by the above-named authors show the effect of pulping and washing on the stability of nitro-cellulose:—

	COLLODION COTTON.		GUN COTTON.	
	1 hour. c.c.	2 hours. c.c.	1 hour. c.c.	2 hour c.c.
Half pulped	—	—	6·1	—
Fully pulped	0·8	1·7	1·5	2·8
Five changes of hot water	0·7	1·7	0·9	2·2
Fifty changes of hot water	0·7	1·5	0·8	2·4

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* *Z. angew. Chem.*, 1904, pp. 982, 1018, 1074.

The presence of moisture in the nitro-cellulose increases the instability under the heat test: thus, a nitro-cellulose containing 1·97 per cent. of moisture yielded 2·6 c.c. of NO per gram, while the same material with 3·4 per cent. of moisture evolved 50 c.c. per gram. Traces of free sulphuric or nitric acids render the material very unstable. Extraction with alcohol for a short time only very materially increases the stability.

The stability of nitro-cellulose is influenced by the materials with which it may be mixed. Alkaline substances, *e. g.* sodium carbonate, etc., render it more stable.

Zinc oxide, which is often used in celluloid mixings, according to H. Nishida,* reduces the stability of the product, although the temperature of ignition is not materially influenced.

Other effects of zinc oxide noted by this observer are that the cubical contraction is diminished as the zinc oxide is increased, the density of the product is the mean value, the tensile strength and modulus of elasticity are lowered—the latter considerably—the hardness of a mixture containing 15 per cent. of zinc oxide was only about half that of the pure celluloid, while the specific resistance fell from 122·5 for the pure celluloid to 28·3 for the product containing 15 per cent. of zinc oxide.

W. Will † tested a large number of samples of celluloid and celluloid articles and also celluloid prepared from stabilized nitro-cellulose by himself. His method consisted in heating 0·1 gram of the product in a lightly closed test tube heated in an oil bath slowly, the rise in temperature being about 5° per minute, and noting the point at which fumes are evolved. Good samples of celluloid do not evolve fumes below 160° C., but with some samples this occurred at as low as 124° C.

According to Will, celluloid is a fairly stable substance, not being affected by shocks, friction, electric sparks, or heating to 100° C. In a few instances, however, the material decomposed at a temperature such as that in contact with an electric light bulb. Compact cellulose burns without explosion, but powdered celluloid can be exploded by electric sparks when in contact with air. The explosions which sometimes accompany fires in celluloid factories or storage places are due to the gases evolved on heating. Celluloid heated out of contact with air yields considerable quantities of carbon monoxide, methane, and hydrogen, which mixed with air form a highly explosive mixture. Burned in a limited supply of air a large proportion of nitric oxide and a small amount of hydrocyanic acid are found in the products of combustion. These substances being poisonous render the fires at celluloid works highly dangerous to the firemen engaged in suppressing them.

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* *Caoutchouc et Gutta-percha*, 1915, pp. 8576, 8592.

† *Z. angew. Chem.*, 1906, p. 1377.

B. Pfyl and P. Rasenack* also refer to the numerous instances of poisoning at celluloid fires, and give details of two series of experiments which they carried out to determine what gases were evolved. (1) By heating the celluloid rapidly until explosion or sudden evolution of gas took place, this being done in an atmosphere of inert gas (CO_2 or N) in air at atmospheric pressure, and in a vacuum. (2) Heating gently so that decomposition took place without explosion.

The products formed from 100 grams of celluloid exploded out of contact with air consisted of:—

Carbonic acid (CO_2)	3000–4000 c.c.
Carbon monoxide (CO)	7000–9000 c.c.
Nitrogen (N)	500
Hydrocyanic acid (HCN)	0·7 gram.
Nitric oxide	Also present.
Acrolein	
Camphor	
Total gases	17,000–18,000 c.c.

In contact with air nitric peroxide (N_2O_4) was formed, which reacting on the acrolein gave rise to very strongly reducing substances, probably derivatives of hydroxylamine. With excess of air carbonic acid, water, and nitrogen were the sole products of explosion; no hydrocyanic acid or carbonic acid are formed on burning celluloid, but in a limited supply of air hydrocyanic acid is produced to the extent of 1·2 grams per 100 of celluloid.

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* *Arbb. Kais. Gesundh. Amt.* 1909, 1; *Chem. Zeit.*, 1909, 763.

A. Panzer* has also examined the products formed by burning celluloid in a vacuum, the celluloid being ignited by an electrically heated wire from which the current was shut off as soon as the material commenced to burn. Under these conditions 24·8 per cent. of the weight of the celluloid was evolved as gaseous products and 16·8 per cent. was left as a kind of charcoal, the remaining 58·4 per cent. of solid and liquid products which had distilled off being difficult to collect and examine. The charcoal was highly pyrophoric, especially after gentle heating, no doubt due to its extremely porous state.

The gases consisted of by volume :—

	per cent.
Nitric oxide	51·1
Nitrous oxide	5·5
Carbonic acid	6·8
Carbonic oxide	30·9
Hydrogen	0·9
Nitrogen	4·8

The liquid products were largely composed of nitric acid and camphor, probably existing as camphor nitrate, $2C_{10}H_{16}O,N_2O_5$.

P. Obermüller † has devised an apparatus for testing the stability of nitro-cellulose by measuring the pressure of the gases generated on heating. This apparatus is shown in Figs. 67 and 68, Z being the decomposition vessel, consisting of a small glass tube having a capacity of about 12 c.c. and with a mark at 5 c.c. This is connected by means of a bent tube, T, which is ground on to it, to the pressure gauge, M, to which is attached a movable mirror scale, S, and also to a vacuum pump through the tubes H and H′, which are provided with stopcocks. By raising or lowering the bulb, G, the mercury may be brought always to the same mark, so that a constant volume may be attained. The decomposition tube is heated by a calcium-chloride bath, which is covered with a layer of paraffin oil to retard evaporation, the bath being enclosed in a sheet-iron casing provided with a window of thick glass for observation purposes. The nitro-cellulose to be tested is pressed till it contains 30 to 35 per cent. of water. About two grams of the sample, which has been rubbed through a 2-mm. mesh sieve, are placed in the decomposition tube and pressed down by the glass rod until

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* *Z. angew. Chem.*, 1909, 1831.

† *Berl. Begirkisverein des Ver. deutsch. Chem.*, Oct. 11, 1904. *Journ. Soc. Chem. Indt.*, 1905, 347.

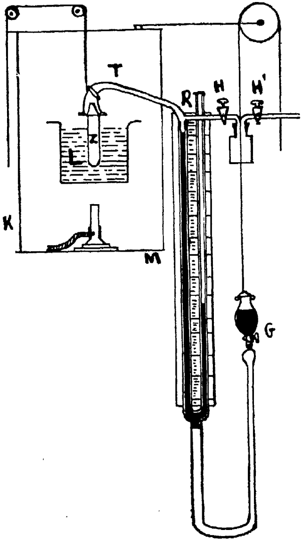
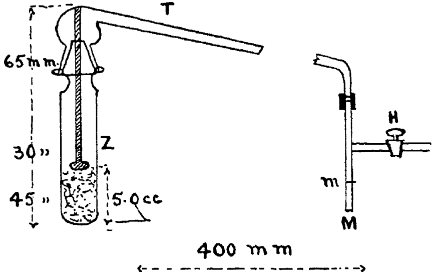


Fig. 67.—Obermüller's Apparatus.

it occupies the volume of 5 c.c., the glass rod being left in the tube. The apparatus is then connected with the pump until the air is completely evacuated when the stopcock, H¹, is closed. The decomposition tube is then placed in the bath which has been heated to 140° C., and after heating about ten minutes the water which has condensed in the left limb of the pressure gauge is driven over into the small receiver between H and H¹ by raising the mercury receiver, G. The mercury in this limb is adjusted to the mark, and the scale moved, so that the zero mark is exactly opposite the surface of the mercury in the right limb. After fifteen minutes heating, the tap H is closed and the first reading is taken, the mercury being brought to the mark again by raising the reservoir, and the difference in pressure read off on the scale. At stated time intervals this is repeated, the mercury being in all cases brought to the mark in the left limb and the pressure read off. Two samples of nitro-cellulose—(1) A sample of collodion cotton, containing 12·4 per cent. of nitrogen, and solubility in ether-alcohol 98 per cent.; and (2) a sample of gun-cotton, containing 12·9 per cent. of nitrogen, and solubility in ether-alcohol 8 per cent.—gave the following results when tested in this way:—



[FIG. 68.—Obermüller's Apparatus.

Time. Minutes.	Collodion Cotton.		Gun-cotton.	
	Pressure. mm.	Increase of Pressure mm.	Pressure. mm.	Increase of Pressure. mm.
0	0	—	0	—
15	15	15	19	19
30	31	16	41	22
45	51	20	66	25
60	75	24	95	29

Viscosity of Celluloid Solutions.—The viscosity of nitrocellulose solutions is a very important property, especially so in the materials for lacquer manufacture and the preparation of artificial silk.

There are many different forms of viscosimeters, but it is somewhat difficult to decide which is the best. It would, however, simplify matters if some form of apparatus were decided upon and the determinations always performed with that particular instrument, in which case results by different observers could be compared with one another. It would also be an advantage to calculate all results to absolute viscosity in C.G.S. units, using some liquid, the viscosity of which has been accurately determined, as a standard and the figure obtained with it as a constant in all subsequent calculations.

Such well-known viscosimeters as Ostwald's, Redwood's, and Engel's, need no description; these depend upon the time of efflux of a measured volume of the liquid. The Bausch and Lamb instrument is a form of torsion instrument depending upon the retarding influence of the liquid, and there are others.

H. Schwarz * recommends two simple methods suitable for factory control, the one, applicable to very viscous liquids, consisting in timing the fall of a glass sphere 7 to 8 grams in weight, through a column of liquid 30 c.m. in depth. Thinner liquids are tested by the time of flow of the liquid from a bulb pipette, which has two marks

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* *Trans. Chem. Ind. Kolloide,* 1913, 32.

—one above and the other just below the bulb—and comparing this with water.

A form of the falling sphere viscosimeter, which is easy to make and simple to use, is described by W. H. Gibson and Miss L. M. Jacobs,* and was used successfully by

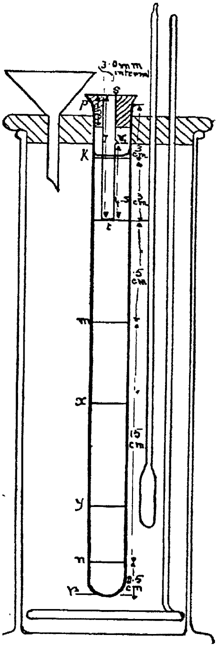

FIG. 69.—Falling-sphere Viscosimeter.

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* *Journ. Chem. Soc.*, "Proceedings 1920," p. 473.

them in the determination of the viscosities of various cellulose products in solution. This viscosimeter is shown in Fig. 69 and consists of a tube, *t*, 2 cm. diameter and 29 cm. in length, divided into four equal lengths of 5 cm., provided with rubber stopper in which is fitted a short piece of glass tube 3 mm. diameter and 7 cm. long, which has a small opening, *v*, just below the stopper. The tube is fitted into the wooden cover of a large gas jar, which is provided also with a thermometer, stirring rod, and filling funnel.

The test is carried out by filling the jar with water, which is brought to the temperature of the experiment. The liquid to be tested is placed in the tube, *t*, up to the mark, *k*; a small steel ball, 1·5 mm. ($= \frac{1}{16}''$) in diameter (the smallest used for ball bearings), is now dropped through the small tube, any air which it might carry with it passing out through the side opening. The time of fall of the ball through the three lower divisions is noted, and from this the absolute viscosity of the liquid can be calculated. The authors use castor oil as a standard fluid, but glycerine, or any other liquid, the viscosity of which is accurately known, may be employed. The viscosity found with castor oil in the instrument described at 20° C. was 9·9, the specific gravity of the oil being 0·96 and that of the steel ball 7·65.

The calculation of the viscosity is based on the equation given by Stokes for the velocity of a sphere falling vertically in a fluid which is—

$$V = \frac{2}{9} gr^2 \frac{S - \sigma}{\eta},$$

where V is the velocity of the sphere, r the radius, and S the density of the sphere, and σ the density and η the viscosity of the liquid.

This equation, however, only applies under certain conditions which are described by the authors, but by using spheres of equal radius in tubes of the same dimensions, a simple equation such as that used for the

Ostwald type of capillary viscosimeter gives the absolute viscosity of the liquid—

$$\frac{\eta}{\eta_1} = \frac{(S - \sigma)\, T}{(S - \sigma_1)\, T_1}.$$

When the time of fall in another liquid of known viscosity has been determined in the tube the absolute viscosity of any solution can thus be calculated.

One of the first points to be noticed about the viscosity of nitro-cellulose solutions is their great variations. Viscosity is related to molecular complexity, and there is no doubt that in solutions of high viscosity the molecular complexes are comparatively large; it is possible to trace a direct connection between the viscosity of such solutions and the mechanical and chemical treatments to which it has been subjected.

As stated by E. R. Chrystall,* "In general the viscosities of nitro-cellulose solutions are diminished by all treatment which the substance or its raw material undergoes, such as bleaching and cleaning the cellulose, stabilizing the nitro-cellulose by boiling, heating the nitrating mixture or the finished product, and beating or exposing to light the solutions under investigation. The presence of traces of impurities in all stages of the work also adversely affects the viscosity. These causes, as well as fundamental differences in the nitro-cellulose itself account for the varying and discordant results obtained by different workers."

H. Schwarz has shown that the "ageing" of nitro-cellulose solutions leads to lowered viscosity, although this is not so apparent in dilute as in strong solutions. The solutions in camphorated spirit have greater viscosity than those of equal strength in ether-alcohol (4 to 3), and these latter in turn are more viscous than solutions in acetone. In camphorated spirit the viscosity is less with a higher concentration of camphor. For certain purposes solutions with high viscosity are desirable, but in others where great fluidity may be required, a low viscosity is preferable. Addition of acids and salts usually lower the viscosity, a fact which was utilized by Lehner in making solutions for the manufacture of artificial silk. Urea in low concentration, *i.e.* 1 per cent., increases the viscosity of solutions of nitro-cellulose by 10 to 15 per cent., but further additions have no appreciable effect. Schwarz also states that as the result of practical experience it has been found that well-dried collodion cotton dissolved in a 75 per cent. solution of camphor in alcohol in the proportions 1 : 12·5 works more easily on the rolls as its viscosity falls.

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* British Association: *First Report on Colloid Chemistry and its Industrial Applications*, 1917, pp. 82, 84.

C. Piest * also points out that solutions of nitro-cellulose in acetone become less viscous on standing, and that this occurs without any deposition of insoluble matters. He also says that the solutions are less viscous according to the amount of bleaching the original cellulose has been subjected to, which he ascribes to the presence of impurities such as esters of oxycellulose derived from the β-cellulose by the action of the bleaching agents.

For further information see the references given in the footnotes to this chapter and also those quoted in the British Association Reports.*

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* British Association : "Cellulose Nitrates." *Second Report on Colloid Chemistry and its General and Industrial Applications*, p. 61.

INDEX

Abel method for gun-cotton, 20
Acetic anhydride, action on cellulose, 17
Acetone, 65
Acid, nitric, specific gravity of, 68
—— sulphuric, specific gravity of, 67
Acids, action on cellulose, 11
—— as solvents for nitro-cellulose, 58
Act. Ges. f. Anilinfabr., patent substitute for camphor, 56
Aeroplane "dopes," 155
"Ageing" of nitro-cellulose solutions, 179, 180
Alcohol, amyl, 64
—— ethyl, 62
—— methyl, 64
Alcoholic solution of camphor for nitro-cellulose, 76, 80
Aldehydes as solvents for nitro-cellulose, 59
Alkalies as solvents for nitro-cellulose, 58
American camphor, 50
Amyl acetate, 65
—— alcohol, 64
Analysis of celluloid, 163–180.
Andemar's patent for artificial silk, 90
Anti-fouling varnish from celluloid, 140
Apparatus for moulding celluloid, 118–121
—— Obermüller's, 174–175
Arbezcarme's patent substitute for camphor, 56
Artificial camphor, 47, 53
—— fibres, 91, 103
—— silk, Brounert on, 90, 96, 97
—— —— Brounert's patents, 102, 103
Artificial silk, Chardonnet's patents, 91–96, 98
—— —— denitration of, 95, 96
—— —— Foltzer on, 90, 98
—— —— Lehner's patents, 99–102
—— —— manufacture of, 90–104
—— —— Pauly's patent, 102
—— —— rendering uninflammable, 95
—— —— waterproofing, 98
—— teeth, celluloid for, 117
Artner's method of manufacturing collars, cuffs, etc., 142
Aylsworth's patent for rendering celluloid uninflammable, 150

Badische Anilin und Soda Fabrik's patents for camphor substitutes, 58, 61
Balls, celluloid, making, 126, 127, 130–133
Barnwell and Rollason's patent for paints and varnishes, 70
Baros camphor, 51
Barthélemy, estimation of camphor in celluloid, 168
Basler & Co.'s patent for use of borneol, 56
Bayer & Co.'s patent substitute for camphor, 56
Béchamp's patent for denitrating artificial silk, 96
Behál's patent for use of borneol, 55
Benzine, 66
Benzol, 66
Bergmann on solubility of nitro-cellulose, 154
—— and Junk, stability of nitro-celluloses, 170
Bèthisy, Fouchard and Vignes' patent for rendering celluloid uninflammable, 151

Bleaching nitro-cellulose, 45
—— —— Spill's patent, 46
Bockmann, analysis of celluloid, 169
Boehringer und Söhne's patent substitutes for camphor, 57
Bolton's celluloid varnish, 159
Borneo camphor, 37, 47, 51
Borneol, 47, 51
—— Basler & Co.'s patent, 56
—— Behál's patent, 55
Böttger and Otto on nitro-cellulose, 69
Bottle varnish, celluloid, 161
Bracconot on nitro-cellulose, 69
Bracconot's Xyloïdine, 69
Bradford Dyers Assoc. and Krais' patent for "Schreinering," 104
Breteau and Lerouse's patent substitutes for camphor, 58
Breuer's patent for artificial silk, 99
British and Continental Camphor Co.'s patent substitutes for camphor, 61
British Association Reports, 180
Bronnert on artificial silk, 90, 96, 97
Bronnert's patents for artificial silk, 102, 103
Brush-making, celluloid in, 108
Buchstab's patent substitutes for camphor, 58

Camphol, 51
Camphor, 47–53
—— alcoholic solution of, for celluloid, 76, 80
—— American, 50
—— artificial, 47, 53
—— Borneo, 37, 47, 51
—— distillation, 49
—— estimation in celluloid, 166–169
—— extraction, 48
—— menthene, 47
—— properties of, 51
—— refining, 50
—— substitutes, 54–58
Casting compositions, celluloid, 133
Castor-oil, 63
Celluloid, analysis of, 163–180
Celluloid, apparatus for moulding, 118–121
—— application of, 108–146
—— articles, casting, 133
—— —— colouring, 141
—— —— pressing hollow, 128
—— for artificial teeth, 117
—— balls, making, 126, 127, 130–133
—— in brush-making, 108
—— collapsible seamless vessels of, 125
—— collars and cuffs, 142
—— combs, 115
—— Co's. patent, 60
—— and cork composition, 145
—— cutting, 111
—— Dobler on, 3
—— dolls, 140
—— examination of, 163–180
—— films, 145, 146
—— historical account of, 69
—— imitation Florentine mosaic, 136
—— industry, 109
—— lacquers, 155–162
—— manufacture, 69–89
—— —— by aid of heat and pressure, 78
—— —— Hyatt's process, 78
—— —— Tribouillet's process, 79
—— —— Walter D. Field on, 30
—— —— with solutions of camphor, 80
—— Manufacturing Co.'s plant, 28
—— metallic incrustations on, 135
—— moulding, 111, 118–121
—— ornaments, 108, 135
—— pens, 141
—— phonograph cylinders, 138
—— posters, 128
—— printing blocks and stamps, 122
—— —— on, 141
—— producing designs on, 134
—— Prof. Reuleaux on, 3
—— properties of, 105–107
—— rendering uninflammable, 147–151
—— for ship's-bottoms, 140
—— solutions, viscosity of, 176–180

Celluloid, stability of, 171
—— stick handles, 138
—— stoppers, 155
—— substitute, 144
—— —— for glass, 121
—— testing, 171
—— treatment of, 108–146
—— umbrella handles, 112, 113, 138
—— varnishes, 155–162
—— working by cold process, 114
—— working by warm process, 115
Cellulose, 8
—— acetates, 17, 18
—— action of acetic anhydride on, 17
—— action of nitric acid on, 11
—— —— reagents on, 10
—— composition, 9
—— di-nitrate, 16
—— esters, 11
—— hexanitrate, 14
—— nitrates, 11–17
—— —— general reactions, 17
—— —— Vielle's experiments, 13
—— pentanitrate, 15
—— tetranitrate, 16
—— thio-carbonate, 18
—— tri-nitrate, 16
—— Xanthogenate, 18
Centrifugals, 24, 33
—— nitrating, 33
Chardonnet's denitrating process, 95
—— patents for artificial silk, 91–96, 98
—— silk, 97
Chemical classification of solvents, 61
Chem. Fab. Greisheim Electron, patent camphor substitutes, 57
Chem. Fab. vorm. Weiler-Ter Meer, patent camphor substitutes, 56
Chrystall, viscosity of nitro-cellulose solutions, 179
Cie. Gen. de Chromolithographie Co.'s spongy celluloid and varnish, 159
Claessen's patent camphor substitutes, 56
Clear films of nitro-cellulose, 155
Clement's patent for rendering celluloid uninflammable, 150
Coach-building, celluloid in, 109
Coal-tar naphtha, 66
Cold process of celluloid manufacture, 80
Collapsible vessels of celluloid, 125
Collars and cuffs, celluloid, 142
Collodion, 158
—— cotton, 19, 35, 69
—— —— methods of preparation, 36
—— silk, 90–104
—— solution, 69
—— wool, 19, 35, 69
Colouring celluloid, 141
Combs, celluloid, 115
Consort. mulhousien patent for artificial silk, 102
Copal in artificial silk, 100
—— varnish, 143
Cotton, collodion, 19, 69
—— composition of, 9, 10
—— gun, 19, 69
—— powder, Schönbein's, 69
Crookes' patent for artificial fibres, 91
Cross and Bevan on cellulose, 10
—— on cellulose acetates, 18
—— —— nitrates, 14
—— —— Xanthogenate, 19
—— viscose, 19
Cross, Bevan and Beadle's patent for viscose silk, 103
Cutting celluloid, 111
Cutting's patent for celluloid films, 70

Denitration of artificial silk, 95, 96
Despeisse's patent for artificial silk, 102
Diluents, 65
Di-nitrate, cellulose, 16
Distillation of camphor, 49
Dobler on celluloid, 3
Dolls, celluloid, 102
Dominte and Merard, solvent for nitro-cellulose, 60
"Dopes," æroplane, 155
Dougal's celluloid varnish, 161
Draper and Tomkins' patent for artificial fibres, 103
Drying apparatus for celluloid, 83–89

Dryobalanops camphora, 51
Dubovitz, analysis of celluloid, 164
Duclaux's patent camphor substitutes, 61
Du Pont de Nemour's patent camphor substitutes, 57, 61

Eckstein's celluloid varnish, 161
Elasticity of celluloid, 107
Electro moulds for celluloid, 114
Esters, cellulose, 11
Ether alcohol, 65
—— ethyl, 65
Extraction of camphor, 48

Falling sphere viscosimeter, 177
Fibres, artificial, 91, 103
"Fibrolithoid," 144
Field on solubility of nitro-cellulose, 153
—— celluloid manufacture, 30
"Fil brilliant," 90
Films, celluloid, 145, 146, 155
Foerster, estimation of camphor in celluloid, 166
Foltzer on artificial silk, 90, 98
France's drying apparatus, 83–89
Fremery and Urban's patent for artificial silk, 102

Gérard's patent varnish, 161
Germain's patent for rendering celluloid uninflammable, 150
Gibson & Jacobs, falling sphere viscosimeter, 177
Gillet's patent camphor substitute, 57
"Glanzstoffe," 90
Glass, celluloid as substitute for, 121
Grange, S de la, coloured celluloid varnish, 160
Gun-cotton, 19
—— Abel method, 20
—— discovery of, 19
—— explosion of, 21
—— Lenk method, 20
—— special for celluloid, 22

Hadow, analysis of celluloid, 164
Hagemann's "Subrit," 145
Hale's patent for manufacture of clear films of nitro-cellulose, 155
Hall's celluloid varnish, 158
Hamecher's apparatus for moulding celluloid, 118–121
Hassac on artificial silk, 97
Herve, estimation of camphor in celluloid, 166
Hexanitro-cellulose, 14
Historical account of celluloid, 69
Hollow celluloid articles, 133
Horizontal mixing machine, 81
Horn, imitation, 1
Hyatt, John Wesley, 2, 74
Hyatt's paper tearer, 27
—— patents for celluloid, 60, 74, 76
—— process for celluloid manufacture, 75
Hyde's patent varnish, 161
Hydraulic press, 25
—— solution strainer, 162
Hydro-carbons as solvents, 59
Hydro-extractor, 21, 24, 26
Hygroscopic solvents, 62

Imitation Florentine mosaic, 136
—— horn, 1
—— inlaid work, 136
—— ivory, 108
—— tortoise-shell, 134
Impressed designs on celluloid, 134
Inflammability of celluloid, 4, 106
Ivory, imitation, 108

Jacob's patent for celluloid stoppers, 155
Jentgen on preparation of nitro-cellulose, 45
Jüterbogk's press, 118

Ketones as solvents, 59
Kinematograph, films for, 145
Knop's use of sulphuric acid, 69
Kodak Co., celluloid films, 145
Koller's celluloid substitute, 144

Lacquers, celluloid, 155–162
Lagneau, Nebel & Vines' patent for rendering celluloid uninflammable, 151
Laurus (*Cinnamomum*) *camphora*, 47

Leather, celluloid as substitute for, 73, 110
Lehner's patents for artificial silk, 99–102
Lehner silk, 96
Lenk method for gun-cotton, 20
Lifting tool for celluloid moulds, 123
Lignin, 10
Lignone complex, 10
Lindsay's patent for "Schreinering," 104
Linseed oil in artificial silk, 100
Lustre cellulose, 90
—— cotton, 90

Machine for tearing paper, 26
Mackintosh's patent solvent for nitro-cellulose, 59
MacNab on preparation of nitro-cellulose, 152
Matteschat on solubility of nitro-cellulose, 154
Maynard's collodion solution, 69
Menthene camphor, 47
Menthol, 47
Mercerizing, 11
Metallic incrustations on celluloid, 135
Methylated spirit, 63
Meyer on printing on celluloid, 142
Mineral matters in celluloid, 165
Mirbane, oil of, 65
Mixing machine, horizontal, 81
—— —— vertical, 82
Mosaic, imitation, 136
Mould frame for celluloid, 123
Moulding celluloid, 111, 118–121
Moulds for celluloid, 112, 113, 118, 119, 123
—— —— umbrella handles 112, 113
—— lifting tool for, 123
Mowbray's method of preparing pyroxylin 37, 44

Naphtha, coal tar, 66
Neupert, printing on celluloid, 143
Nigro and Hollande's patent for rendering celluloid uninflammable, 148
Nishida, stability of celluloid, 171
Nitrates, cellulose, 11–17
Nitrating apparatus, 27, 30, 32
—— centrifugals, 33
—— plant, 27, 30, 32
—— vessel, 30
Nitric acid, action on cellulose, 11
—— —— for denitrating, 95
—— —— in nitro-cellulose making, 11–17, 19–21
—— —— pyroxylin, 60
—— —— specific gravity of, 68
Nitro-benzene, 65
Nitro-benzol, 65
Nitro-cellulose, clear films of, 155
—— Mowbray's process, 37–45
—— preparation of, 11–46
—— press for, 25
—— solutions, "ageing" of, 180
—— solvents for, 58–65
—— stability of, 169–176
—— washing trucks for, 23
Nitro-celluloses, 11–17
Nitrogen, determination in celluloid, 163
Nitrometer, 163
Non-hygroscopic solvents, 62

Obermüller, stability of nitro-cellulose, 173
Obermüller's apparatus 174, 175
Oil, castor, 63
—— of mirbane, 65
Ornaments, celluloid, 108, 135
Ostwald's viscosimeter, 176

Packing, waterproof, 109
Paget's patent solvent for nitro-cellulose, 60
Panzer, gases evolved on heating celluloid, 173
Paper tearer, Hyatt's, 26
Parkes, Alexander, 1, 71
"Parkesine," 1, 71
Parkes' patents, 59, 71, 72
Parkin's patent for rendering celluloid uninflammable, 147
Parkin and Williams' patent for rendering celluloid uninflammable, 150
Pauly's patent for artificial silk, 102
Paville's method of preparing artificial silk, 99

Pelouze, solvent for nitro-cellulose, 60
Pens, celluloid, 141
Pentanitro-cellulose, 15
Petroleum spirit, 66
Pfyl and Rasenack, gases evolved on heating celluloid, 172
Phonograph cylinders of celluloid, 138
Photography, films for, 145
—— use of collodion in, 70
Piest, "ageing" of nitro-cellulose solutions, 180
Plant, nitrating, 27, 30, 32
Poaching machine, 21
Polarimeter, use of, in estimating camphor, 167, 168
Polishing celluloid, 114
Posters, celluloid, 128
Press, hydraulic, 25
—— Jüterbogks, 118
Presses for nitro-cellulose, 25
Pressing celluloid, 128
Printing blocks, celluloid, 122
—— on celluloid, 142, 143
—— process, Meyer's, 142
Properties of celluloid, 105–107
Prost & Les Fils Pinay-jeune, patent for rendering celluloid uninflammable, 148
Prost & Mickey's patent for rendering celluloid uninflammable, 148
Pyroxylin, denitrating, 95, 96
—— employment of, in manufacture of varnishes, 152–162
—— preparing, 22–46

Reagents, action on cellulose, 10
Réaumer on artificial silk, 90
Redwood's viscosimeter, 176
Reichenbach's patent for celluloid films, 145
Reuleaux, Prof., on celluloid, 3
Rhemische Gummi und Celluloid-fabrik printing on celluloid, 143
Riddle's patent solvent for nitro-cellulose, 60

Sayer's patent solvents for nitro-cellulose, 60
Schloesing's method of analysis, 17, 95, 164
—— test for denitration, 95
Schmerber's patent substitute for camphor, 55
Schönbein and Böttger, discovery of gun-cotton, 19
Schönbein's cotton-powder, 69
—— gun-cotton, 69
"Schreiner" finish, 104
"Schreinering," 104
Schupphous' patent solvents for nitro-cellulose, 60
Schwartz, "ageing" of nitro-cellulose solutions, 179
Schwartz's viscosimeter, 176
Scott Archer, use of collodion in photography, 70
Seamless vessels of celluloid, 125
Selmar and Lange's centrifugalizer, 34
Ships' bottoms, celluloid for, 140
Silk, artificial, 90–104
—— Chardonnet's, 97
—— collodion, 90–104
—— Lehner, 96, 99–102
Soc. Anon. Nouvelle L'Oyonnithe patent substitute for camphor, 57
Soc. Civ. des Pellicules patent for celluloid films, 146
Solubility of nitro-cellulose, 154
Solution, collodion, 69
Solvents, hygroscopic, 62
—— for nitro-cellulose, 59–62
—— non-hygroscopic, 62
—— of pyroxylin :—58–65
    acids, 58
    alcohols, 59
    aldehydes, 59
    alkalies or basic substances, 58
    chemical classification, 61
    esters, 59
    general classification, 61
    hydrocarbons, 59
    ketones, 59
    patents, 59–61
    terpenes and derivatives, 59
    Walter D. Field on, 61
Specific gravity of celluloid, 105
—— —— nitric acid, 68
—— —— sulphuric acid, 67

Spill, Daniel, 2
Spill's patents, 59, 72–74
Spirit, petroleum, 66
—— wood, 64
Spongy celluloid, 159
Stability of nitro-cellulose, 169–170
Staines Celluloid Co.'s process, 30
Stamps, celluloid, 122
Stearn's patent for artificial silk, 103
Stevens' patent solvents for nitro-cellulose, 60
Stevens' patent for rendering celluloid uninflammable, 148
Stick handles, celluloid, 112–114
Stirrer for acid mixing, 29
Stocker's uninflammable celluloid, 149
Stoppers, celluloid, 155
Strehlenert's patent for waterproofing artificial silk, 98
Streubel's "vegetaline," 144
"Subrit," Hagemann's, 145
Substitute, celluloid, 144
—— for glass, 121
Substitutes, camphor, 54–58
Sulphuric acid, Knop's use of, in nitro-cellulose making, 69
—— —— specific gravity of, 67
Surgical bandages of celluloid, 110
Swan's patent for artificial fibres, 91
Swinburne's patent for artificial fibres, 91

Tearing paper, machine for, 26
Teeth, celluloid, 117
Tensile strength of celluloid, 107
Terpenes and derivatives as solvents for pyroxylin, 59
Testing celluloid, 171
Tetranitro-cellulose, 16
Thieme's patent substitute for camphor, 56
Thio-carbonate, cellulose, 18
"Tiger's Eye," imitation, 139
Tortoise-shell, imitation, 134
Treatment of celluloid, 108–146
Tribouillet and Besancéle's nitrating. apparatus, 23
Tribouillet and Besancéle's process of celluloid manufacture, 22–26, 97
Trinitro-cellulose, 16
Tschevschner's celluloid varnish, 158

Umbrella handle, 112, 138
—— —— mould for, 112, 113
Uninflammable celluloid, 147–151
Utz, estimation of camphor in celluloid, 168

Varnish, anti-fouling, 140
—— copal, 143
Varnishes, celluloid, 155–162
—— pyroxylin, 155–162
"Vegetaline," Streubel's, 144
Vereinigte Glanzstoffe-Fabriken patent for artificial silk, 102
Vertical mixing machine, 82
Vessel, nitrating, 30
Victoria enamel, 156
Viscose, 19, 103
—— silk, 103
Viscosimeters:—
    Engel's, 176
    Falling sphere, 177
    Ostwald's, 176
    Redwood's, 176
    Schwartz's, 176
Viscosity of celluloid solutions, 176–180
Vivier's artificial silk, 99
Von Koretz on camphor winning, 48

Warm process for celluloid, 115
Washing trucks for nitro-cellulose, 23
Waterproof packing, celluloid, 109
Waterproofing artificial silk, 98
Weston's patent for artificial fibres, 91
White and Schupphous nitrating plant, 30–32
Will's method of testing celluloid, 171
Wolfram, Dr. Guido, on solvents, 62
Wood naphtha, 64
—— spirit, 64

Wood spirit in celluloid manufacture, 71
Wool, collodion, 19, 35, 69
Wynne & Powell's patent for artificial fibres, 91, 103

Xanthogenate, cellulose, 18
Xyloïdine, Braconnot's, 69
Xylonite, 72, 144

Zapon enamel, 156

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